AD_____

Report No. WCDC 6667

EFFECT OF PHASE CHANGE IN SOLID-SOLID REACTIONS

. Final Report

by

Joseph H. McLain
Michael D. McClure

April 1968

DEPARTMENT OF THE ARMY

EDGEWOOD ARSENAL

Research Laboratories

Chemical Research Laboratory

Edgewood Arsenal, Maryland   21010

Grant DA-AMC-18-035-77(A)

Department of Chemistry
Washington College
Chestertown, Maryland   21620

DDC

APR 4 1969

CLEA 'INGHOUSE

Distribution Statement

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Commanding Officer, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when no longer needed. Do not return it to the originator.

IN REPLY REFER TO·

SMUEA-TSTI-T   6 March 1969

SUBJECT: Notice of Change and/or Clearance of Report

TO: Headquarters
           Defense Documentation Center
           Cameron Station
           Alexandria, Virginia 22314

       Changes noted below in subject report are submitted for your
information and necessary action.

Report No: Final Report.   ▆▆▆▆▆▆▆▆▆▆

Title: Effect of Phase in Solid-Solid Reactions

Contract No.
Author(s):DA-AMC-18-035-77(A)

Originating Agency: Washington College, Department of Chemistry

Cleared by DOD: Stamp No. 5, 24 February 1969

Remarks: This report has been cleared for release to the general public,

provided the following references are deleted with India ink: Ref. 8 and 22 on

page 65; Appendix C, starting on page 98, Ref. 3, 6, 12, 45, 46, 61 and 62.

After deletions have been made insert distribution 1 and forward to CFSTI

          FOR THE DIRECTOR:

          JOHN A. GARBER, JR.
          Chief, Technical Releases Branch
          Technical Information Division
          Technical Support Directorate

Report No. WCDC 6667

EFFECT OF PHASE CHANGE IN SOLID-SOLID REACTIONS

Final Report

by

Joseph H. McLain
Michael D. McClure

April 1968

DEPARTMENT OF THE ARMY

EDGEWOOD ARSENAL

Research Laboratories

Chemical Research Laboratory

Edgewood Arsenal, Maryland 21010

Grant DA-AMC-18-035-77(A)

Project 1C014501B71A

Department of Chemistry
Washington College
Chestertown, Maryland 21620

Sanitized Version

FOREWORD

The work described in this report was authorized under Project 1C014501B71A, Life Sciences Basic Research in Support of Material, Chemical (U). This work was started in October 1964 and completed in October 1967.

The information in this report has been cleared for release to the general public.

Acknowledgements

DIGEST

The effects of phase changes, defect structure, mechanical treatment, moisture content, and doping of the constituents of the potassium chlorate-sulfur system on the reactivity of the system has been investigated by means of differential themal analysis, thermoconducti-metric analysis and burning rates.

The effect of confinement during burning of the fuel mix (potassium chlorate, sulfur and sodium bicarbonate) has also been studied.

Summary of Results:

1. A reaction mechanism for S-KClO$_3$ has been established in which the sulfur liquid-liquid ($\lambda \rightarrow \pi$) phase transition plays an important role.

2. A supersensitive KClO$_3$ (Cu^{++} doped) has been prepared and tested.

3. Moisture content of the reactants have been proven to be extremely important to the reactivity.

4. A new conductivity cell has been designed, fabricated and tested to be satisfactory.

5. The concept of ignition temperature has been discussed and clarified.

6. A new ignition equation has been derived and applied.

7. Confinement by increase in K factor during burning of the untreated fuel mix in tubes has been shown to lead to detonation.

8. Previous treatment of the KClO$_3$ (and the sulfur but to a much lesser degree) such as grinding and change of crystal growth has been shown to affect reactivity.

Conclusions:

A. The mechanism of the KClO$_3$-S reaction is independent of the decomposition of the KClO$_3$. It is, however, dependent upon the lattice "looseness" of the KClO$_3$ and its permeability to the sulfur molecules. Untreated KClO$_3$

- 3 -

reaches the required looseness at the temperature at which sulfur undergoes a liquid-liquid phase transition.

B. Copper and copper alloy tools and screens should be removed from $KClO_3$ operations as a safety measure.

C. Thermoconductimetric measurements are of real value in the study of reactivity of solids.

D. Burning rate measurements are of little value in the study of reactivity of this system.

E. The previous treatment of the constituents (notably $KClO_3$) such as mechanical, thermal treatment, defects of all types play a measurably important role in the stability of the system.

F. The moisture content of the system is extremely important. The rate of the $KClO_3$-S reaction is a maximum at some low percentage of moisture ($0.5 \pm 0.3\%$).

G. The hardness of crystalline solids should be studied further to serve as an indicator of reactivity.

H. The growth of burning-to-detonation of fuel mix ($KClO_3$-S-$NaHCO_3$) is profoundly enhanced by a large K factor in the munition.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

EFFECT OF PHASE CHANGE IN SOLID-SOLID REACTIONS

I. Introduction

The overall object of this research is shown by the title. The system $KClO_3$ - S - $NaHCO_3$ was selected for exploration in considerable depth. However, additional systems have been included during the past three years so that certain results with the original system could be enlarged upon or confirmed.

After embarking upon this research we found out very shortly that the scope of investigation needed to be broadened to include virtually all of the factors that affect reactivity of solids, such as moisture content, thermal history, doping defects, mechanical treatment, etc. In all probability, the efficacy of these factors in affecting reactivity is due to their roles in either aiding or deterring phase transitions.

The remainder of this report will attempt to describe the effects studied, the experimental techniques where new and/or substantially different, some theory which points the way to further work, and our results and conclusions.

The presentation has been made by making an outline of effects studied which is followed by results of this research and how each of the factors influences the $KClO_3$-S-$NaHCO_3$ mixture.

II. Factors That Affect Reactivity of Solids

A. Hedvall Effect

J.A. Hedvall[3] stated "whenever solid substances undergo a transformation involving the rearrangement of their atoms they pass through a state in which they are more reactive than in the initial or final state."

Examples of this is found in the reaction temperature work of Hedvall, Hüttig and other solid state chemists of the early 1900's.

Specifically, the reaction temperature of CaO with several different ionic solids are as shown:

Reaction Temp., °C

$CaO + CuSO_4 \longrightarrow CaSO_4 + CuO$ 515

$3\ CaO + Co_3(PO_4)_2 \longrightarrow Ca_3(PO_4)_2 + 3CaO$ 520

		Reaction Temp., °C
$CaO + MgCO_3 \longrightarrow CaCO_3 + MgO$		525
$CaO + MnSiO_3 \longrightarrow CaSiO_3 + MnO$		565
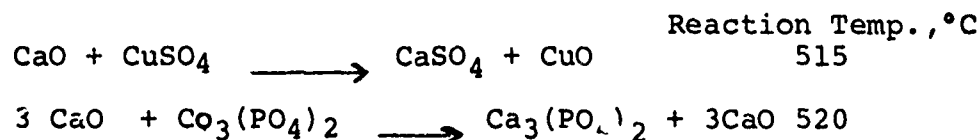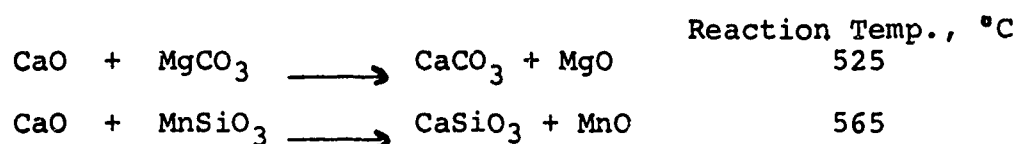
Why are these temperatures all so close together? Hedvall would explain this by saying that CaO has a characteristic temperature which it must attain before it can react rapidly with another solid and that this temperature is near the point at which the CaO lattice undergoes a rearrangement. The literature shows CaO to undergo a phase transition at 415 - 430°C. The reaction $6CaO + 5SO_{2(g)} \longrightarrow 5CaSO_3 + CaO$ does not go at below 400°C but goes rapidly at 418°C.

Reaction temperatures for $AgNO_3$ with CaO, BaO, SrO, show the following:

	Reaction Temperature °C
$AgNO_3 + CaO \longrightarrow$	164
$AgNO_3 + SrO \longrightarrow$	172
$AgNO_3 + BaO \longrightarrow$	170
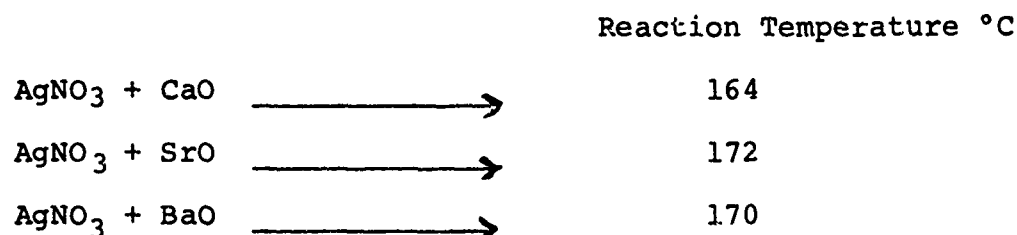
The reaction temperature in this example is controlled by the $AgNO_3$ which has a phase transition at 160°C.

B. Tammann Temperature

G. Tammann[4] published a thermodynamic analysis in which he related the reaction temperatures of Hedvall and others to an ionic mobility factor as follows:

If α represents the ratio of the absolute temperature of an ionic solid to its melting point in degrees absolute then surface mobility becomes active at $\alpha = 0.3$ and lattice diffusion requires $\alpha = 0.5$ or higher.

Tammann temperatures and the Hedvall effect are intimately related in that a Tammann temperature may represent some lattice transformation other than solid to liquid. Furthermore, there must be a considerable amount of mobility attained by lattice units before a phase transition can take place. An outstanding example of this is AgI which has a melting point of 552°C and $\alpha = 0.5$ at 139°C. The literature[5] reports AgI yellow hexagonal $\longrightarrow$ AgI orange cubic at 138°C to 150°C. Thus, the Tammann temperature coincides with the transition temperature at which AgI would be more reactive.

- 10 -
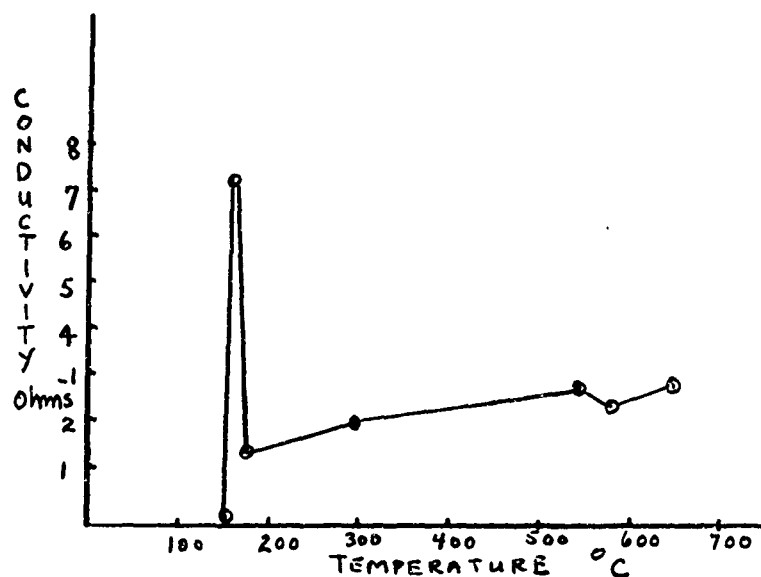
Figure 1

Conductivity vs. Temperature For $AgI-B_2O$

The increased reactivity of AgI with BaO to form BaI_2 is shown in the following graph to coincide closely with the Tammann temperature at the transition point.

Figure 2
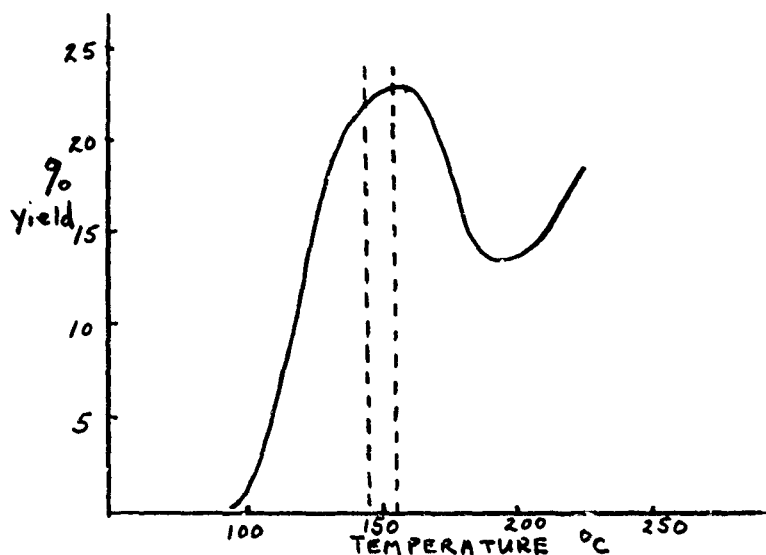
Diagram illustrating the enhanced reactivity in the region of phase transformation (Hedvall effect)

Tammann temperatures, as could be expected, also exert a profound effect on the conductivity of solids. Using AgI as the example again, conductivity measurements show a 20,000 factor increase in the temperature interval from 142.4° to 146.5°C.

C. Moisture

Inasmuch as the water content of an ionic lattice will come off under heating, additional interior and exterior surface will result just from its displacement. There may be an added erosive factor on the lattice, as well as a possible flux effect.

Water content plays an important role in phase transitions _per se_ as shown in the following example of NH_4NO_3 by Nagatani and Seiyama[6].

Ammonium nitrate normally, in a DTA thermogram, shows the following phase transitions at the temperatures noted:

IV to III: Rhombic I to Rhombic II at 32.1°C

III to II: Rhombic II to Tetragonal at 84.2°C

II to I: Tetragonal to Cubic at 125.2°C

I to melt   169.6°C

Yet at very low moisture contents it is possible to by-pass the IV to III transition and go directly from Rhombic I to Tetragonal. Also, small amounts of moisture absorbed by NH_4NO_3 cause large downward shifts of transition temperatures, such as 36°C on the 84.2°C transition temperature.

Nagatani and Seiyama (v.s.) made the statement that "it is not the moisture content which brings about this shift but the change in speed of the transition." Thus if moisture affects the speed of the transition under constant heating rate the temperature must be affected. Also, the speed must be affected on a more physical than chemical basis probably by flux or surface increase.

D. Defects

Because all solid-solid reactions are diffusion controlled the reacting solids cannot be perfect or there would be nothing to diffuse or no place to diffuse to.

There are two types of inherent defects, Frenkel and Schottky and four types of nonstoichiometric defects as follows:

Type I	Anion vacancies	-	n type
Type II	Interstitial cations	-	n type
Type III	Interstitial anions	-	p type
Type IV	Cation vacancies	-	p type

The effects of the nonstoichiometric type of defects are more pronounced and more conducive to control.

There is only one proven example of the effect of defects on burning-type reactions known to the writers. However, additional research is being performed in addition to this work, and confirmation of the theory already exists in that the properties of solids can be altered immensely by minute amounts of dopant. The literature is replete with studies of the effects of dopant on such properties as catalytic activity conductivity and temperatures of decomposition.*

The theory is, briefly, that the oxidizing component of an oxidizing-reducing reaction such as PbO in $2PbO + Si \longrightarrow SiO_2 + 2Pb$ can be made a better oxidizer (a better attractor for electrons) by creating positive holes in its lattice. By the same token the reducing agent can be made a better reducer (a better donor of electrons) by doping in such a manner as to make it an n type (excess of electrons) conductor.

The known example mentioned previously is from some work done at the U.S. Naval Ammunition Depot, Crane, Indiana[7] in which the CuO, PbO_2, Si starter mix was found to be much faster when a silicon containing traces of Mn and Cr was used.

F. Mechanical Activation

The influence of mechanical activation on the reactivity of solids is discussed in some detail in Reference (2). However, for the purpose of unity in this report, it should be sufficient to state that there is ample

---

*For specific references see those in "Literature Cited" References 1 and 2 vide supra.

evidence to show that solids can be made to react faster
at lower temperatures by grinding or other rigorous
mechanical treatment. This has been proven to be differ-
ent than the surface area effect and is explicable by
either strain energy and/or by defect creation.

F. Confinement

The rate of reaction of most solid mixes is
influenced greatly by the ambient pressure, particularly
those which have gaseous products so that additional pres-
sure is created as the reaction propagates. The influence
of pressure on solid state transitions is also well known.

The growth of rates of reaction to "runaway" velo-
cities and the role of confinement has been discussed
previously in Reference (2).

The influence of pressure effects during burning
is shown by the following experiment.

One pound rocket motors were burned while under
an applied stress. Stresses were applied by means of a
centrifuge in three attitudes as shown by the diagram
below:
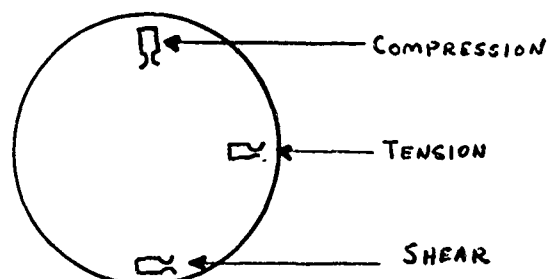
The acceleration force was 100 gravitational units.
A typical formulation was:

NH_4NO_3	74% by weight
"C" Rubber	14%
Guanidine nitrate	6%
Melamine	3%
$(NH_4)_2C_2O_4$	3%

Under tension this mix showed a 20% decrease in
average pressure for static burning. Under compression

there was a 35% increase and under shear there was a 17% decrease. Some ten variations of mix were used and in all cases applied stress caused more progressive burning and the slower the burning rate the more sensitive the mix to stress.

G. Crystal Form

It is known that crystal form plays an all important role on sensitivity and rate of reaction for many compounds such as lead oxide and RDX. Some data on sensitivities of various crystalline forms of HMX are shown below. (Reference 8).

	form	form	form	form
System –	orthorhombic	monoclinic	monoclinic	hexogonal
Habit –	rods & needles	needles	plates	rods
Impact Sensitivity --	2-30	1-33	1-20	1-10

H. Thermal Treatment

1. Inherited Defects

An example of the effect of previous treatment which is of considerable importance in reaction rates is Fe_2O_3.

It has been proven by X-ray methods that Fe_2O_3 prepared by ignition of $Fe_2(SO_4)_3$ at temperatures below 650°C retains a great deal of structural looseness. $Fe2O3$ prepared by ignition of $Fe(OH)_3$ or $Fe_2(C_2O_4)_3$ does not show the same structural looseness upon X-ray examination.

Hedvall and Sandberg[9] performed the following experiment.

A sample of Fe_2O_3, made from the sulfate which had an average particle size considerably larger than a competitive Fe_2O_3 made from $Fe_2(C_2O_4)_3$, was tested for reactivity with CaO. The results obtained are shown in the figure below.

Figure 3

Reactivity of Fe_2O_3 Preparations
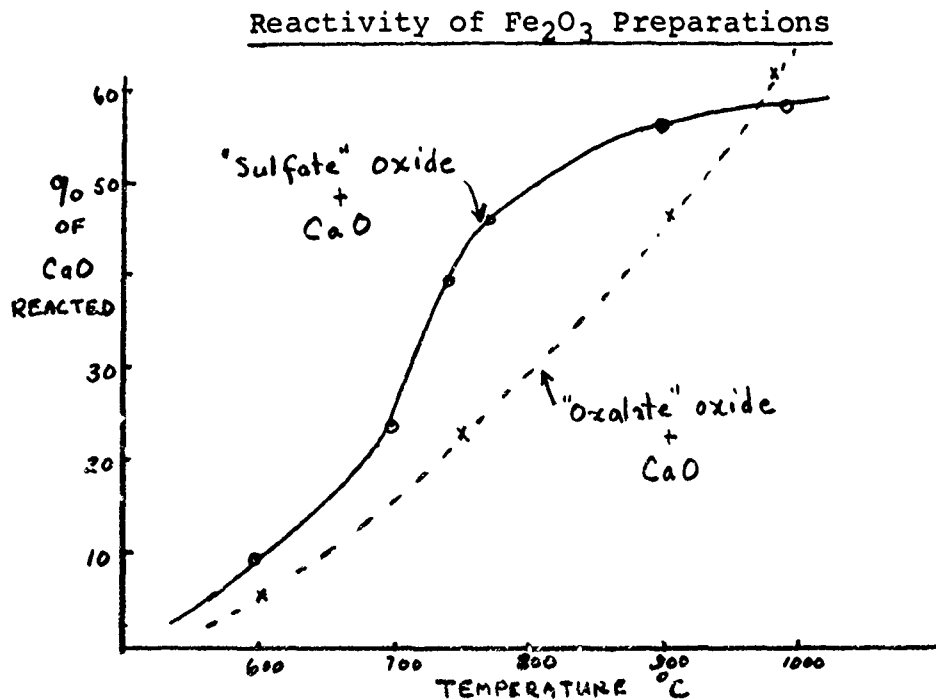
It can be seen from the above data that 2 times as much CaO reacted with the "sulfate oxide" than with the "oxalate oxide" at 750°C even though the "oxalate oxide" was of small particle size.

This difference makes itself felt in the ignition temperatures of Fe_2O_3-Ti mixes. "Sulfate oxide" ignites readily from primer flash. Hydroxide or oxalate oxide does not.

One other fact is demonstrated by these data. It can be seen from the figure that the two curves intersect at slightly above 900°C and the "oxalate oxide" now is more reactive than the sulfate oxide presumably because of its greater surface area and because the ions of the "sulfate oxide" have attained sufficient mobility to equalize the structures.

This is confirmed by an experiment in which the "sulfate oxide" was heated at 900°C for thirty minutes and the X-ray examination then gave the same sharp patterns as had been obtained for the less active "hydroxide oxide." After this annealing, it too gave the same reactivity as the less reactive forms.

- 16 -

2. Annealing

Although the term annealing is generally used by metallurgists for removing strains from metallic lattices it can be applied to ionic lattice strains as well.

An outstanding example is that of Pryor and Evans[10] the results of which are summarized in figure 4.

Figure 4
Relation between temperature of ignition and percentage dissolution of Fe_2O_3 in 0.1N HCl at 25°C.
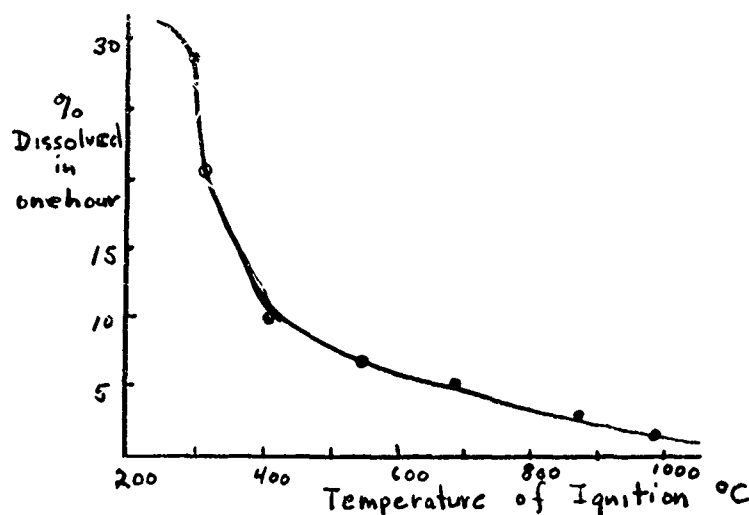
As can be seen from the data, this work tends to confirm the previous work of Hedvall in that at 900°C the lattice is more dense and less reactive. The components of the lattice have been given enough kinetic energy to allow them to migrate to the steady state lattice position.

I. Irradiation

Although no work on irradiation has been done on this grant, the effect of irradiation on the defect properties is well known. Irradiation of solids has been used to enhance or inhibit solid state materials in catalysts and other related fields.

X-ray, neutron, and ultraviolet beams have been used in many ways. Work done by Freeman and Anderson[11] has shown that the properties $KClO_4$ and NH_4ClO_4 can be greatly altered by irradiation.

The use of beams of metal vapor and the halogen gases, although not irradiation, can also be used to increase the defect structure making "f" centers and "V" centers in that order.

III. EXPERIMENTAL METHODS AS APPLIED TO THE FACTORS THAT AFFECT REACTIVITY.

A. Hedvall Effect

I. Reaction Temperatures

The Hedvall Effect was derived from "reaction temperature" measurements which were carried out with large masses of material in the early part of the century. "Reaction temperature" may be defined as follows.[12] In the exothermic reaction of solids,* the heat of reaction is first of all dissipated to the surroundings. A point is reached, however, when this is no longer possible, and the temperature of the reaction rises appreciably. This increases the reaction rate, which in turn, accelerates heat evolution. The reaction proceeds thus uncontrolled until it is slowed by the accumulation of solid products or runs out of reactant. The temperature at which an "uncontrolled" increase in rate begins is the reaction temperature and is readily obtained from the graph showing the temperature of the bulk of the mixture when heated slowly under controlled conditions.

2. Differential Thermal Analyzer

The advent and standardization of the differential thermal analyzer, has allowed reaction temperatures to be determined much more accurately with very small quantities and has helped to determine the role of product coatings and critical mass. It has also been able to show very clearly the role of transitions and the occurrence of a "preignition reaction" (P.I.R.) which denotes the true reaction temperature at a given heating rate.

The DTA is of great importance to the study of pyrotechnic and explosive material because it not only reveals endothermic reactions important to the reactivity, but the exothermic reactions and their slope which signal the approach of an explosion. Thermograms of such materials

---

*All solid-solid reactions must be exothermic from the second law of thermodynamics, $\Delta G = \Delta H - T\Delta S$ because, if solids A and B react to give solids C and D the entropy change, $\Delta S \cong 0$. Thus for the reaction to proceed, ($\Delta G =$ negative) the change in enthalpy (ΔH) must be negative or exothermic.

should be much more mandatory than impact tests or ignition temperature tests by the Henkin-McGill technique.[13]

3. Thermoconductimetric Analysis. (TCA)

A large portion of the experimental effort of this research has gone into the development of solid state conductivity measurements and their interpretation. For the first time, conductivity measurements have been carried out continuously on a system (PbO-Si) to ignition. These data and their interpretation were presented in reference (2).

This year's work in this area has been devoted largely to the perfecting of a new cell and the measurement of some new systems. J. Rose[12] makes the following statement about electrical conductivity studies of solids. "Though this method is valuable in the case of single crystals of alkali halides it is not of great use at present (1961) in other cases. There are certain difficulties inherent in the use of powders. For instance, there is no certain method of distinguishing between bulk and surface conductivity, or between electronic and ionic conductivity without elaborate experimental techniques. Some qualitative results have, however, been obtained (14),(15),(16) and the method is likely to be fruitful in the future."

As reported previously[2] in this work, the authors agree with Rose on the difficulties inherent in the use of powders such as have been used by Jen Chiu[15] and Berg and Burmistrova[16]. Consequently, we have done all of our measurements on high density pellets made by vacuum pressing at 10,000 to 20,000 pounds per square inch.

We believe the method to be a valuable one particularly in the field of oxidation-reduction reactions such as

$$2PbO + Si \longrightarrow SiO_2 + 2Pb$$

wherein the reaction products are much more conductive than the reactants, or reversed systems such as

$$2Fe + 3BaO_2 \longrightarrow Fe_2O_3 + 3BaO$$

or $\quad 2Fe + 3BaO_2 \longrightarrow 2BaO + BaFe_2O_4$

wherein the products are much less conductive than the reactants.

However, the usefulness of thermoconductimetric analysis is not confined to the above systems as has been shown by our work on $NiSO_4.7H_2O$ pellets and by Freeman and Rudloff[17] from their work on $KClO_3$ pellets, and quite definitely the method can show transition changes and signal the Hedvall Effect.

B. Tammann Temperature

The DTA is of first importance as a method for determination of Tammann temperatures. However, TCA can also be used. Freeman's[17] work on $KClO_3$ which explains the drop in conductivity in the temperature range 25°C to 125°C can be explained alternatively by saying that when $KClO_3$ is given enough heat energy to allow it to anneal (that is, have its ions sink to their equilibrium lattice positions), "frozen-in" disorder is relieved and a less defective crystal is obtained. Minimum conductivity and presumably maximum order is obtained by Freeman at 85°C or 358°K which is an α of 0.55.

This work has used both DTA and TCA for Tammann temperature determinations.

C. Moisture

DTA has been used exclusively to study the effect of moisture on the reaction.

D. Defects

DTA, TCA and burning rate determinations have been used to determine the effects of defect type and concentration. DTA has been used predominately on the systems $KClO_3$ and S; and $KClO_3$, $NaHCO_3$ and S. TCA has been used on the system PbO and Si.

Rate of burning determinations have been performed with both and are summarized in reference (2). The effects of doping, and crystal defects have been shown to be measurable by rates of burning technique.

E. Mechanical Activation

DTA was used successfully to show that recently ground $KClO_3$ crystals are more reactive than those that have been annealed. Also, rates of burning were used to determine the effect of mechanical activation on PbO

(yellow) to PbO (red), however, the rates of burning were not as sensitive a probe to determine the effects of recent grinding.

F. Confinement

Rates of burning experiments with $KClO_3$-S-$NaHCO_3$ (fuel mix) were used to show the great importance of confinement in causing a burning reaction to increase its pressure and temperature so that self heating increases the velocity of the reaction to runaway speeds and detonation.

G. Crystal Form

DTA was used to measure the effects of changes in reactivity of the $KClO_3$-S system when the $KClO_3$ crystalline habit was changed by use of dopants and changed crystallization media. See reference (1).

H. Thermal Treatment

DTA used on the $KClO3$-S system and DTA and TCA used with the PbO-Si system.

I. Sensitivity

DTA, TCA, and Henkin-McGill[13] ignition temperatures were used. Activation energies were approximated from the ignition temperature data. Also, these data were used for two new ignition parameters, minimum spontaneous ignition temperature (S.I.T. min.) and maximum spontaneous ignition temperatures (S.I.T. max.).

In the field of pyrotechnics, propellants and explosives, sensitivity is approximated by an 'ignition temperature'. In other less spectacular fields of solid state chemistry, sensitivity is sometimes equated and measured by reaction temperatures. In all cases, sensitivity is really a measure of the reactivity of a system under some kind and quantity of stimulus, whether the stimulus be heat, friction, impact or others.

The problem of sensitivity in practice generally resolves itself to a "Hobsons Choice" between systems which are sensitive enough to work when and as needed but insensitive enough to be safe to mix and load.

An immense amount of work, experimental as well as theoretical, has been done in the area of sensitivity (ignition temperatures). See Appendix C of this report for references in this area.

Believing that it is of utmost importance to a
study such as this that we understand the kinetics of
Solid-Solid Reactions, the authors have made a detailed
and rigorous study of ignition theory and have given
some applications of the theory to the system under study.
Much of the experimental work was done in the second
year of the grant and the data is reported in reference(2).

IV. RESULTS AND CALCULATIONS

A. Hedvall Effect

The importance of the liquid S_8 to liquid S_3
phase transition of sulfur ($\lambda \rightarrow \pi$) to the reaction of
$KClO_3$ and S was demonstrated in the first year's work[1].
A reaction mechanism was postulated at the end of the
first year which stated, in essence, that because the
normal $KClO_3$ lattice did not react with sulfur until the
S_8 molecules broke up into smaller fragments the reactivity
of the system was dependent upon the porosity or inner
surface of the $KClO_3$.

As a consequence of this postulate, $KClO_3$ crystals
were doped with a series of dopants and it was found
that the $KClO_3$ lattice could be made porous enough to
have room temperature pre-ignition reactions which were
exothermic enough to cause heat up to detonation.

This lattice porosity hypothesis was confirmed
still further by the work of the second and third years.

B. Tammann Temperature

1. $KClO_3$-S System

Work done in the second year showed that
freshly ground $KClO_3$ was more sensitive to heating than
material that had been held at a temperature greater
than 0.55 of the melting temperature of the $KClO_3$ in degrees
absolute.

2. Nickel sulfate heptahydrate $NiSO_4.7H_2O$

TCA studies were made on pellets of hydrated
nickel sulfate and the data obtained are summarized in
Figure 1, Appendix A.

3. PbO-Si System

Thermoconductimetric studies[2] on the
litharge-silicon system showed that there was a change

- 22 -

in slope at 0.5 times the transition temperature and that ignition took place at 307°C which is just 0.5 times the melting point of PbO. This data is presented in Figure 2, Appendix A.

C. Thermoconductivity Cell

Due to the belief of the authors that thermo-conductimetric analysis[1] is a valuable tool for detecting changes in lattice mobility and onset of reaction, as well as experiencing an ignition[2] of a PbO-Si (80-20) pellet, and inasmuch as there is nothing available commercially, we set out to design and build a stronger and more useful cell.

A number of alterations on the basic design[2] have been made to correct difficulties which have arisen.

A water condenser (Figure 3C, Appendix A) was placed on the vacuum line to keep the temperature of the copper tubing low enough so that the rubber tubing from the vacuum apparatus could be used.

When the electrometer[1] was connected to the electrodes for a test run, it was observed that an extremely large amount of 60 cycle pick-up was resulting in false readings. The AC voltage was measured between ground and the cell and was found to be dependent on the heater potential. In order to eliminate this difficulty the cell was grounded to the water lines.

The electrodes were potted into the spark plug bases by using "Insulment" ceramic potting compound, which on continued heating cracked and caused air leakage. In an effort to plug the cracks, we tried (Dow Corning) silastic bathtub caulking compound. This gave acceptable vacuum properties, but destroyed the high resistance which is necessary between the electrodes and spark plug casing.

Subsequent to the loss of high resistance, the electrodes were removed from the spark plug casing and repotted using an asbestos-cement washer (Figure 3A, Appendix A) in place of the mica washers. The potting was done with Insulment, adding small amounts at a time and oven drying at 60°C. The asbestos washer was used instead of mica to give the electrodes increased support during the potting process. This alteration gave good vacuum properties, but was found to have too low a resistance to be of use.

The electrodes were removed from the spark plug casing again and sealed in a pyrex glass glove (Figure 3b, Appendix A) with Insulment. The glass covered electrodes were then sealed into the hexagonal base using Insulment and heat.

Due to the difference in the coefficients of thermal expansion the glass gloves cracked on strong heating and loss of vacuum followed. Also the resistance went way down.

The electrodes were again broken down and a design was proposed using ceramic tubing to cover the electrodes, but it was felt that this design would fail because Insulment would have to be used for potting. From the results of the previous modifications, as well as data collected on the insulating properties, it was concluded that Insulment broke down on heating, thus becoming a semiconductor and contributing to the loss in resistance.

It is easily seen from the above discussion that a new design for the electrodes was needed.

Since a spark plug is already designed to give high resistance between electrode and casing at high temperature, the following design was proposed and adopted on an experimental basis.

Part of the base of two Champion W-18 spark plugs was cut off. The spring loaded electrode was cut down in length and silver brazed to the center electrode of the spark plug.

The screw adjustable electrode was cut down in length and silver brazed to the shortened center electrode of the second spark plug. The center electrode was shortened after first exposing it by breaking away some of the ceramic isulation.

While this modification of the W-18 spark plug was being performed we visited the largest insulator plant in the East and talked to their service engineer about high resistance at high temperatures potting compounds. His recommendation was a Sauereisin cement.

We obtained a material which, had we had it to start with, would have eliminated the delays and problems. This material is called Sauereisin Electrotemp Cement No. 8 and it has the following properties.

Electrical resistivity 25 to 600°C $>$ 1×10^{10} ohms
                        650 to 850°C 1.3×10^9 ohms
                        850 to 900°C 7.1×10^8 ohms

Dielectric strength shows 270 volts per mil at a temperature of 500°F.

It is specifically designed for spark plugs, heating elements and coating resistors and it withstands thermal shock.

The final electrode structure is shown in Figure 3d, Appendix A.

It has been used this year for nine determinations from ambient temperature to 430°C and has shown no sign of breakdown. The data obtained have been extremely reproducible and are of real value in the exploration of solid phase reactions.

D. Moisture Effect

Seven desiccators were established according to last year's[2] design and were

Number	%H_2SO_4	R.H.
1	100.00	0.0
2	77.63	3.2
3	69.09	8.5
4	45.26	47.2
5	21.38	88.8
6	7.68	97.5
7	0.00	100.0

placed in the constant temperature room at 24°C for three days before beginning the study.

The master batch of fuel mix, prepared in June of 1966, was dried for two days in an oven at 60°C before starting this study.

A DTA (using a duPont 900 differential thermal analyzer) was run on the master batch of fuel mix after the two days of oven drying and this thermogram was designated as the zero hour study.

DTA's and quantitative analysis were made on samples from each of the desiccators at: 24 hours, 48 hours, 72 hours, 120 hours, 15 days, and 31 days.

The quantitative analyses were made by determining the ratio of the weight of the oven dried (at 60°C for three days) sample to the weight of the sample removed from the desiccator. This was then converted

$$\frac{\text{wgt of oven dried sample}}{\text{wgt of desiccator sample}} \times 100\% = \% \text{ Purity}$$

to percentages and recorded in Table 1.

TABLE 1
Percent Purity

Time	0%	3.2%	8.5%	47.2%	88.8%	97.5%	100%
zero hrs.	----	----	----	----	----	----	----
24 hrs.	99.53	99.45	99.48	99.44	99.43	99.53	99.33
48 hrs.	99.55	99.38	98.96	99.06	99.18	98.70	98.65
72 hrs.	99.46	99.45	99.35	99.40	99.55	98.78	98.13
120 hrs.	99.99	99.98	99.99	99.75	99.76	98.93	97.45
15 days	99.46	99.34	99.35	99.41	99.44	----	----
31 days	99.56	99.56	99.38	99.60	99.56	----	----
Avg.	99.59	99.53	99.45	99.44	99.49	98.99	98.39

The 97.5% and 100% RH studies were terminated after the 120 hour sample due to the collection of a large volume of water in the sample container.

A percent purity determination was run on a sample of the fuel mix after it had predried for two days in the oven. This was done to see if there was any loss in weight due to sulfur volatilization. The results calculated by the manner described above gave

Purity = 99.91%

As one would expect, the average value of the purity goes down as the relative humidity goes up. Note that the purity levels are off for the 8.5%, 47.2%, and 88.8% relative humidities. This leveling is the result of totally hydrating the fuel mix and accounts for the similarity between the 8.5% and 47.2% thermograms. It is not until the RH is raised high enough to dissolve the

mix that we see a change in the purity (97.5% and 100% RH). It should be pointed out that the percent purity as well as the thermal data for the 88.8% study are very hard to explain since they do not fit into the pattern.

A few words must be said about the effect of storage on the basic fuel mix. The components were freshly ground, dried, and screened at the beginning of last year's study and a D.T.A. was run. After storage for one year and two days of oven drying (60°C) another D.T.A. was run. These two thermograms are shown in Figure 4, Appendix A.

Note that the ignition temperature[2] (see Tables 2 and 3) of the June 66 run is 164°C (147° + 17°C instrument recalibration correction) and that there are two secondary exotherms. On the June 67 run the ignition temperature is 170°C and there are no secondary exotherms. The reactivities are $R_{66}' = 7.1$[2] and $R_{67}' = 5.85$ for the respective years. (See Figures 19 and 20, Appendix A for reactivity plots).

Two possible explanations for the differences are: first, over the year's storage time the microfine particles which resulted from recent grinding have reacted. It would be these small particles which account for the low ignition temperature while particles of larger sizes account for the secondary exotherms.

The second explantion is that over the year the mix had picked up moisture from the atmosphere and on oven drying has undergone recrystallization. This recrystallization would account for the increase in ignition temperature and the higher temperature would add sufficient energy so that the mix would react all at once with no secondary exotherms.

Storage at 0% RH (Figures 5 and 6, Appendix A) -- Note the change in structure of the thermograms between the zero and 24 hour studies. This increase in reactivity is believed to be in line with the work done on flare compositions[2] in which it was ascertained that the reactivity of the mix reaches a maximum at about 0.1% H_2O! The structure of the 24 hour thermogram is the same as that of last year's; i.e., a low temperature preignition reaction resulting from the flux action of the water, a $NaHCO_3$ endotherm and a second exotherm due to the reaction of larger particles at the higher temperature. Once again, as time increased and the water content goes down, the reactivity goes down (ignition temperature increases).

Storage at 3.2% RH (Figures 7 and 8, Appendix A) -- In all cases at this humidity this year's ignition temperatures are higher than last year's. Thus, due to the increase in temperature one would expect from kinetics that the reaction go much faster and show only one exotherm and no endotherm. Again, we must stress that we have started this study with a less reactive mix then the one used in last year's study. The structure of the 48 hour thermogram can be explained on the basis that the mix is picking up H_2O and becoming more reactive. Then at 72 hours the water is acting as a recrystallizing solvent rather than as a flux agent and thus the reactivity goes down. The increase in reactivity of the 15 day study is not understood. Finally, as the water content goes up the reactivity goes down.

Storage at 8.5% RH (Figures 9 and 10, Appendix A) -- Note how all the thermograms up through the 72 hour study have the $NaHCO_3$ (increased reactivity) endotherm which is due to the flux action of water. At 120 hours the water content is so high that recrystallization occurs and results in a decrease in reactivity (increase in ignition temperature).

Storage at 47.2% RH (Figures 11 and 12, Appendix A) -- Again we see that the ignition temperature at first decreases and then increases. This is the first study in which the 31 day ignition temperature is above that of the zero hour sample and can be explained on the basis of recrystallization.

Storage at 88.8% RH (Figures 13 and 14, Appendix A -- In this study the water content is so high (extreme recrystallization) that the reactivity is greatly decreased and we actually see the $NaHCO_3$ decomposition begin before the $KClO_3$ and S start reacting.

Storage at 97.5% RH (Figures 15 and 16, Appendix A) -- Note the appearance of the large water endotherms starting at 24 hours and the disappearance of the $NaNCO_3$ endotherms. The disappearance of the endotherms is reasonable since the ignition temperatures in this study are below those in the 88.8% R.H. study but whey they have decreased is unknown.

Storage at 100% RH (Figures 17 and 18, Appendix A) -- Note the large water endotherms in this study and also the reappearance of the $NaHCO_3$ endotherm in the 72 and 120 hour studies. Again we see that the ignition temperature in this study increases with time to a level well above the 170°C zero-hour temperature.

TABLE 2

Effect of Storage at Varying Humidities on Ignition Temperatures (1967)

Time	0%	3.2%	8.5%	47.2%	88.8%	97.5%	100%
0 hrs.	170	170	170	170	170	170	170
24 hrs.	145*	166	155*	160	187	178	175
48 hrs.	185	152*	155*	158	180	185	170
72 hrs.	170	166	133*	130	178	170	187
120 hrs.	162	157	170	145*	182	170	181
15 days	163	148*	168	168	190	---	---
31 days	168	168	170	175	190	---	---

TABLE 3

Effect of Storage at Varying Humidities on Ignition Temperature (1966-after 17°C recalibration correction) [2]

Time	0%	3.2%	8.5%	47.2%	88.8%	97.5%	100%
0 hrs.	164	164	164	164	164	164	164
24 hrs.	152*	157	142*	147*	147▲	172	177
48 hrs.	147	137*	152*	137*	157	172	172
72 hrs.	172	147*	172	157	152▲	182	177
120 hrs.	152	147*	142*	162	162	167	197
15 days	177	147*	172	162	157	192	182
31 days	162	152*	172	177	177	---	---

Comparing the zero hour and 31 day temperatures between the two tables we see that the final (31 day) temperatures for the 0% and 3.2% studies are less than the beginning temperatures, that the beginning and final temperatures for the 8.5% study are nearly the same, and that

the final temperatures for the 88.8%, 97.5%, and 100%
studies are greater than the beginning temperatures.

Also note that in every case, except the 1966
study at 88.8%, where the ignition temperature is 155°C
or below (marked by *) the thermograms have the highly
structural pattern of a preignition exotherm followed
by a decomposition endotherm of the NaHCO$_3$ followed by
a second exotherm. In the case of the 1966 s' 1y at
88.8% RH (maked by 4) we do not see the above ; ·tern
but we do note that their structure is very m1 .ι dif-
ferent for those observed for ignition temperatures of
160°C or above.

Whether or not the above observation can be in-
terpreted as meaning a detonation might occur if the
ignition is raised above 160°C, is to say the least,
dubious, but certainly it is more possible at the higher
temperature.

Some confirmation of our findings about the effect
of moisture has just been reported by Freeman and Rudloff[17]
whose conductivity-temperature measurements on KClO$_3$ pellets
showed high conductivity of pellets containing moisture
in the 25-125°C range compared to dried pellets measured
in a vacuum.

E. Ignition and Rates of Burning

The onset of an exothermic reaction with enough
liberation of energy*is called ignition. Sensitivity to
ignition is a measure of reactivity and in fact ignition
temperature data have been used to calculate a "quasi
activation energy." See reference 2. Also in reference
(2) these data have been critically reviewed and two
novel applications of the data presented (S.I.T. min.
and S.I.T. max.).

The authors believe that it is of utmost importance
in research on solid state reactions and reactivity that
an analytical model of the ignition mechanism be developed
and defined. A search of the literature was carried out.

---

*See reference (2) for a definition of ignition.

The results of this search are listed in Appendix C of
this report.* As might be expected because of its im-
mense practical interest in the past decade, most of the
theoretical work on ignition has been carried out by
workers in the solid propellant area. We have reviewed
this literature thoroughly and could not find a compre-
hensive derivation of the equations. In consequence,
therefore, we performed such a derivation and have added
some ideas with the expectation that our ideas can be
developed still further and result in considerable pro-
gress.

D.M. Johnson[18] has made a theoretical approach
to ignition of pyrotechnic compositions in which he de-
fines Ti (ignition temperature) as that temperature to
which a given solid composition must be heated to ignite
and continue to combust without further heating by an
external source. Johnson's approach starts with the
basic equation for heat transfer derived as follows:

The basic equation for heat transfer

$$\frac{\partial T}{\partial t} = \propto \frac{\partial^2 T}{\partial x^2} \quad (1)$$

can be derived as follows:

Consider a slab ABCD of substance bounded by a re-
gion of high temperature T_2 and a region of low temper-
ature T_1

---
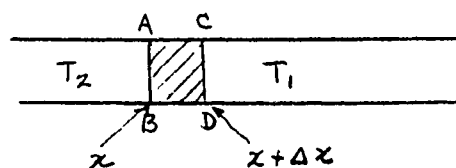
*It should be noted that although we heard from three dif-
ferent sources that Professor G.B. Kistiakowsky had solved
this problem, a search by government personnel at the
Ballistics Research Laboratory Library, and of the "open"
literature gave negative results. The authors wrote to
Professor Kistiakowsky and posed the question and he replied
that he had no recollection of ever doing anything pertinent
to our problem. Although the following treatment is in
its outline and direction due principally to D.M. Johnson,[18]
the authors take responsibility for its extensions, math-
ematical analysis and expository additions.

- 31 -

Heat(H) flows into the slab from AB to CD because of the temperature difference. Thus the change in heat content of the slab with time(t) must be the difference in the heat flow in and the heat flow out or

$$-KA\frac{\partial T}{\partial x}\Big|_{x} + KA\frac{\partial T}{\partial x}\Big|_{x+\Delta x} = \frac{\partial H}{\partial t} \qquad (2)$$

$K = $ coeff. of thermal conductivity

but

$$\frac{\partial H}{\partial t} = \left(\rho A \Delta x C\right)\frac{\partial T}{\partial t} \qquad (3)$$

where $\rho = $ density
$A = $ area
$\Delta x = $ thickness
$C = $ specific heat

Substituting eq.(3) into eq.(2) yields

$$-KA\frac{\partial T}{\partial t}\Big|_{x} + KA\frac{\partial T}{\partial x}\Big|_{x+\Delta x} = \left(\rho A \Delta x C\right)\frac{\partial T}{\partial t} \qquad (4)$$

Performing a Taylor's Series expansion of the second term on the left hand side of eq(4) we get

$$-KA\frac{\partial T}{\partial x}\Big|_{x} + KA\left\{\frac{\partial T}{\partial x}\Big|_{x} + \frac{\partial^2 T}{\partial x^2}\Delta x\right\} = \left(\rho A \Delta x C\right)\frac{\partial T}{\partial t} \qquad (5)$$

Cancellation and rearrangement of (5) gives

$$K \cancel{A}\frac{\partial^2 T}{\partial x^2}\cancel{\Delta x} = \left(\rho \cancel{A} \cancel{\Delta x} C\right)\frac{\partial T}{\partial t}$$

$$K\frac{\partial^2 T}{\partial x^2} = \rho C \frac{\partial T}{\partial t}$$

$$\frac{\partial T}{\partial t} = \frac{K}{\rho C}\frac{\partial^2 T}{\partial x^2} \qquad (6)$$

Let $\dfrac{K}{\rho c} = \alpha$ diffusivity, then (6) becomes

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (1) \quad \text{the } \underline{\text{heat equation}}.$$

     If we assume ideality of ignition, i.e. entire surface of slab is ignited simultaneously and that there are no radiant losses of heat and the container does not contribute to the conduction of heat, then it should be possible to determine the temperature of the slab at any given time by constructing a solution to the heat equation.

     A solution to the heat equation is as follows: Let the temperature (T) of the slab be a function of some variable (y) so that

$$T = T(y) \quad\quad\quad (7)$$

and let y be defined as

$$y = x t^n \quad\quad (8)$$

where "x" is a position coordinate and "t" is time.

     Calculating $\dfrac{\partial T}{\partial t}$ and $\dfrac{\partial^2 T}{\partial x^2}$ and equating them through the "heat equation"(1) with the restriction that any xt products that appear may be made some power of y. Thus

$$\frac{\partial T}{\partial t} = \left(\frac{\partial T}{\partial y} \right)\left(\frac{\partial y}{\partial t} \right) \quad (9)$$

but $\dfrac{\partial y}{\partial t} = n x t^{n-1}$ (10) substituting (10) in (9)

$$\frac{\partial T}{\partial t} = \frac{\partial T}{\partial y} \cdot n x t^{n-1} \quad (11)$$

Now calculating $\dfrac{\partial^2 T}{\partial x^2}$

$$\frac{\partial T}{\partial x} = \left(\frac{\partial T}{\partial y}\right)\left(\frac{\partial y}{\partial x}\right) \quad (12)$$

$$\frac{\partial^2 T}{\partial x^2} = \left(\frac{\partial^2 T}{\partial y^2}\right)\left(\frac{\partial y}{\partial x}\right)^2 + \left(\frac{\partial T}{\partial y}\right)\left(\frac{\partial^2 y}{\partial x^2}\right) \quad (13)$$

$$\frac{\partial y}{\partial x} = t^n \quad (14)$$

$$\left(\frac{\partial y}{\partial x}\right)^2 = t^{2n} \quad (15)$$

and $\quad \dfrac{\partial^2 y}{\partial x^2} = 0 \quad \left(\text{refer to (14) and (8)}\right) \quad (16)$

Making the appropriate substitutions of (16) and (15) into (13) then:

$$\frac{\partial^2 T}{\partial x^2} = \left(\frac{\partial^2 T}{\partial y^2}\right) t^{2n} + 0 \quad (17)$$

Now substitute (17) and (11) into the "heat equation"

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (1)$$

$$\left(\frac{\partial T}{\partial y}\right) n x t^{n-1} = \alpha \left(\frac{\partial^2 T}{\partial y^2}\right) t^{2n} \quad (18)$$

Rearranging equation (18) and collecting the "t" terms

$$\left\{ \frac{\partial T}{\partial y} = \left(\frac{\partial^2 T}{\partial y^2}\right)\left(\frac{\alpha t^{2n}}{n x t^{n-1}}\right) \right\} = \left\{ \frac{\partial T}{\partial y} = \left(\frac{\partial^2 T}{\partial y^2}\right)\left(\frac{\alpha}{n x t^{-n-1}}\right) \right\} \quad (19)$$

- 34 -

In the second half of euqation 19 there is an $\mathbf{X}$t product and $\mathbf{X}$ is to the 1st power. Since the restriction was placed that all "$\mathbf{X}$t" products be powers of y then this "$\mathbf{X}$t" product is the 1st power of y and therefore the exponents of the "t" terms must be equal.

or
$$n = -n - 1$$
$$2n = -1$$
$$n = -\tfrac{1}{2} \quad (20)$$

Substituting equation (20) into equation (19) and rearranging yields:

$$\frac{\partial T}{\partial y} = \frac{\partial^2 T}{\partial y^2} \frac{\alpha}{-\tfrac{1}{2} x t^{-\tfrac{1}{2}}} \quad (21)$$

and inasmuch as $y = \mathbf{X}t^n$ then (21) becomes

$$\frac{\partial T}{\partial y} = - \frac{\partial^2 T}{\partial y^2} \frac{2\alpha}{y} \quad (22)$$

or
$$\frac{\partial^2 T}{\partial y^2} = - y/2\alpha \left(\frac{\partial T}{\partial y} \right) \quad (23)$$

Define P as $P = \frac{\partial T}{\partial y}$ then

$$\frac{dP}{dy} = - y/2\alpha \; P \quad \text{and rearranging gives}$$

$$\frac{dP}{P} = - y/2\alpha \; dy \quad (24)$$

integration gives

$$\ln P = - y^2/4\alpha + C_1 \quad (25) \quad \text{or;}$$

$$P = C_1 e^{-y^2/4\alpha} \quad (26) \quad \text{or;}$$

$$\frac{dT}{dy} = C_1 e^{-y^2/4\alpha} \quad \text{which upon integration}$$
$$\text{gives} -$$

$$T = C_1 \int_m^n e^{-y^2/4\alpha} \, dy + C_2 \qquad (27)$$

Let $Z^2 = y^2/4\alpha$ and $Z = y/2\sqrt{\alpha}$ and substitute

$y = x t^n = x t^{-1/2}$ then;

$$Z = \frac{x}{2\sqrt{\alpha t}} \qquad (28)$$

Substitute (28) into (27)

$$T = C_1 \int_m^n e^{-Z^2} \, dz + C_2 \qquad (29)$$

The values of "m" and "n" are obtained by the analysis of (28) as follows:

as $t \longrightarrow \infty$, $Z \longrightarrow 0$

as $t \longrightarrow 0$, $Z \longrightarrow \infty$

as $x \longrightarrow 0$, $Z \longrightarrow 0$

as $x \longrightarrow \infty$, $Z \longrightarrow \infty$

Therefore the lower limit "m" = 0 and "n" can have any value from 0 to ∞, namely, $x/2\sqrt{\alpha t}$.

Equation (29) becomes

$$T = C_1 \int_0^{\frac{x}{2\sqrt{\alpha t}}} e^{-Z^2} \, dz + C_2 \qquad (30)$$

It is now necessary to evaluate the constants C_1 and C_2.

As the time(t) $\longrightarrow \infty$ then $T \longrightarrow$ Ti (ignition temperature) or

$$T_i = C_1 \int_0^0 e^{-Z^2} \, dz + C_2 \qquad (31)$$

where the upper limit has been replaced by zero because

$$\lim Z = 0 \quad as \quad t \rightarrow \infty$$

- 36 -

and T_i must be equal to C_2.

$$T_i = C_2 \quad (32)$$

Equation (30) now becomes

$$T = C_1 \int_0^{x/2\sqrt{\alpha t}} e^{-z^2} dz + T_i \quad (33)$$

If the time (t) $\longrightarrow$ 0 then the temperature T = Ta (ambient temperature) and

$$\lim z = \infty \text{ as } t \to 0$$

Using these boundary conditions, equation (33) becomes

$$T_a - T_i = C_1 \int_0^\infty e^{-z^2} dz \quad (34) \text{ and}$$

$$C_1 = \frac{T_a - T_i}{\int_0^\infty e^{-z^2} dz} \quad (35)$$

Proceeding to evaluate $\int_0^\infty e^{-z^2} dz$ by transforming into polar coordinates.

Let

$$\int_0^\infty e^{-z^2} dz = \int_0^\infty e^{-x^2} dx = \int_0^\infty e^{-y^2} dy \quad (36)$$

then

$$\left[\int_0^\infty e^{-z^2} dz \right]^2 = \left(\int_0^\infty e^{-x^2} dx \right) \left(\int_0^\infty e^{-y^2} dy \right) \quad (37)$$

Rearrange (37) to

$$\left[\int_0^\infty e^{-z^2} dz \right]^2 = \int_0^\infty dy \int_0^\infty e^{-(x^2+y^2)} dx \quad (38)$$

Substitute polar for cartesian coordinates

$$\left[\int_0^\infty e^{-z^2} dz\right]^2 = \int d\theta \int e^{-(r^2\cos^2\theta + r^2\sin^2\theta)} r\, dr$$

$$= \int d\theta \int e^{-r^2(\cos^2\theta + \sin^2\theta)} r\, dr$$

$$= \int d\theta \int e^{-r^2} r\, dr \quad (39)$$

The angle θ can be any value between 0 and $\pi/2$ and r can have any value between 0 and ∞. Thus equation (39) becomes

$$\left[\int_0^\infty e^{-z^2} dz\right]^2 = \int_0^{\pi/2} d\theta \int_0^\infty e^{-r^2} r\, dr \quad (40)$$

Performing the required integrations and then evaluating them yields;

$$\left[\int_0^\infty e^{-z^2} dz\right]^2 = \theta\Big|_0^{\pi/2} \cdot -(1/2) e^{-r^2}\Big|_0^\infty$$

$$= (\pi/2)(-1/2)(0-1)$$

$$= \pi/4 \quad \text{and}$$

$$\int_0^\infty e^{-z^2} dz = \frac{\sqrt{\pi}}{2} \quad (41)$$

From equations (41) and (35)

$$C_1 = \frac{T_a - T_i}{\frac{\sqrt{\pi}}{2}} = 2\frac{\left(T_a - T_i\right)}{\sqrt{\pi}} \quad (42)$$

- 38 -

Substituting (42) into (33)

$$T - T_i = 2 \frac{(T_a - T_i)}{\sqrt{\pi}} \int_0^{x/2\sqrt{\alpha t}} e^{-z^2} dz \quad (43)$$

$$\frac{T - T_i}{T_a - T_i} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\alpha t}}} e^{-z^2} dz \quad (44)$$

where Ti = ignition temperature

Ta = ambient temperature

T = the temperature at some point between x and $x + \Delta x$ in the slab and at some time t.

Ta $<$ T $<$ Ti

x = distance in cm.

α = diffusivity = $\left(\frac{K}{\rho c} \right)$

t = time in seconds

Equation (44) is exact agreement in Johnson's equation (2) page 2 of reference (18) and the required solution to the heat equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (1)$$

To complete this mathematical analysis and prove that equation (44) is a solution to the heat equation it is only necessary to differentiate (44) and see if it satisfies the heat equation. See Appendix B for this proof.

Johnson in his report[18] solves his equation (2) for T and differentiates to get $\frac{\partial T}{\partial x}$ the temperature gradient in the mix.

$$\frac{\partial T}{\partial x} = \frac{(T_a - T_i)}{\sqrt{\pi \alpha t}} e^{-\frac{x^2}{4\alpha t}} \quad (J.3)$$

where $t > 0$

and $0 < x < L$

(L = length of composition)

- 39 -

from the one dimensional heat flow equation

$$q_{in} = - KA \frac{\partial T}{\partial x} = \frac{\partial H}{\partial T} \quad (J.4)$$ substitution of the

$(\partial T / \partial x)$
temperature gradient produces:

$$q_{in} = KA \frac{(T_i - T_a)}{\sqrt{\pi \alpha t}} e^{\frac{-x^2}{4\alpha t}} \quad (J.5)$$

Let C be the specific heat of the composition and de-
fined as

$$c = -\frac{1}{m} \cdot \frac{\partial H}{\partial T} \quad (J.6)$$

and the mass (m) as
$$m = \rho A x \quad (J.7)$$

The appropriate substitutions into (J.4) yields

$$\frac{\partial x}{\partial t} = \frac{K}{\rho c x} = \frac{\alpha}{x} \quad (J.8)$$

It can be seen that equation (J.8) states that
the rate of burning of the composition is directly pro-
portional to the diffusivity ($\alpha = K/\rho c$) and inversely

proportional to the distance (x) from the heat source.

Integrating (J.8) between limits x_0 to x and t_0 to
t where $x \gg x_0$ and $t \gg t_0$ produces

$$x^2 \cong 2\alpha t \quad (J.9)$$

Substitution of the value for x^2 from (J.9) into (J.5)
yields

$$q_{in} = \frac{KA(T_i - T_a)}{\sqrt{\pi e \alpha t}} \quad (J.10)$$

Solving (J.10) for t (the time to ignite) from a constnat
heat flow (q in) gives:

$$t = \frac{K^2 A^2 (T_i - T_a)^2}{\pi e \alpha q_{in}^2} \quad (J.11)$$

- 40 -

but substituting $\alpha = \dfrac{K}{\rho c}$ into (J.11) gives

$$t = \frac{K \rho C A^2 (T_i - T_a)^2}{\pi e \, q_{in}^2} \quad (J.12)$$

Defining ignition energy, E, of a system as

$$E = q_{in} \cdot t \quad (J.13)$$

and substituting into (J.12) yields

$$E = \frac{K \rho C A^2 (T_i - T_a)^2}{\pi e \, q_{in}} \quad (J.14)$$

Equation J.12

$$t = \frac{K \rho C A^2 (T_i - T_a)^2}{\pi e \, q_{in}^2}$$

when subjected to a dimensional analysis balances out.

A physical analysis presents the following:

a. time to ignite is longer if thermal conductivity is high.
b. time to ignite is longer if density is high.
c. time to ignite is longer if specific heat is large.
d. time to ignite is longer if area to be ignited is large.
e. time to ignite is longer if temperature of ignition is high.
f. time to ignite is shorter if igniter output is high.

In view of the above it is quite obvious why the Henkin-McGill[13] times have little chance to be very accurate, because the area and density terms play an important and variable role in this test.

Neither Johnson nor the authors make any claim that the above equation or its modifications are the full story. As a matter of fact, it would be necessary to add some additional terms to the equation to make it more useful. Before proceeding to make this analysis it should be pointed out that the equation does have some application to the field of pyrotechnics as it now stands.

The first of these applications is the difference in ignition energy necessary to ignite a given mix at the extremes in temperature met in munition use.

For a given mix or solid state reaction with a Ti = 300°C, then the time required for ignition at 30°C compared to the time for ignition at -50°C are shown

$$\frac{t_{30}}{t_{-50}} = \frac{(300-30)^2}{(300+60)^2} = \frac{72900}{129600} = .56$$

which shows that only 56% of the energy required at -50°C is required at 30°C.

This effect of temperature on ignition sensitivity has been found to be true for impact tests as well as been shown by Rideal and Robertson[19] and by Ubbelohde et al.[20] In fact, the 50% chance of explosion for varying temperatures is shown as follows for NH_4NO_3.

T°C	25	75	100	150	175(molten)
Kg-inches	62	56	54	54	24

Returning to ignition by heat source and equation J.12 it can be seen that there is an additional effect of ambient temperature. If a first fire or starting composition is used or if a small portion of the mix itself is ignited, the rate of burning or heat supply to the un-ignited mass will be much slower at the lower temperatures. The ignition equation shows that if the rate of q.in is decreased to one half, the ignition time would be increased by a factor of four. Thus, if the two effects are combined, ignition times and ignition energies could be changed by a factor of 600% in the example chosen.

Ignition temperature determinations, by means of the Henkin-McGill technique viewed in the light of the ignition equation, give much more reliable and reproducible values. For example, using the data of Johnson (reference 18) on $BaCrO_4$ - B mix the differences due to sample size, rate of heat application, nature of the container and the test apparatus can be removed to a large extent.

Using the following data

Bath Temperature °C	Time to Ignition (sec)
702	25.6
682	35.6
673	39.4
659	73.5

Heat flow through the boundary layer of molten metal

$$q_1 = \frac{K_1 A (T_B - T_i)}{X1} \quad (J.16)$$

K_1 = thermal conductivity metal

T_B = bath temperature

T_i = temp. of boundary

$X1$ = thickness of molten metal

$$q_2 = \frac{K_2 A (T_1 - Tign)}{X_2} \quad (J.17)$$

where the subscript 2 applies to the cup wall

Rearranging these equations gives

$$T_B - T_1 = \frac{q_1 x_1}{K_1 A} \quad (J.18)$$

$$T_1 - Tign = \frac{q_2 X_2}{K_2 A} \quad (J.19)$$

Adding (J.18) and (J.19)

$$T_B - Tign = \frac{qin.}{A} \left[\frac{X1}{K_1} + \frac{X2}{K_2} \right] \quad (J.20)$$

Substitution of $\frac{H}{t}$ for qin. in equation (J.12) yields

$$t = \frac{H^2 \pi e}{(Tign - Ta)^2} \cdot 2 K \rho C A^2 \quad (J.21)$$

and similarly, substitution of $\frac{H}{t}$ for qin. in (J.20) yields equation (J.22)

$$t = \frac{H}{A(T_B - T\,ign)} \left[\frac{X1}{K_1} + \frac{X2}{K_2} \right] \quad (J.22)$$

Combining these two equations by multiplying gives equation (J.23).

$$t^2 = \left[\frac{H^3 \pi e}{K \rho C A^3 (T_B - T_i)(T_{\eta n} - T_a)} \right] \left[\frac{x_1}{K_1} + \frac{x_2}{K_2} \right] (J.23)$$

which for the type of data obtained in these experiments reduces to

$$t^2 (T_B - Tign) = B, \text{(J.23)} \text{(Mod.)}$$

where $B = \left[\dfrac{H^3 \pi e}{K \rho C A^3 (T_{ign} - T_a)^2} \right] \left[\dfrac{x_1}{K_1} + \dfrac{x_2}{K_2} \right]$

and is a system constant.

By changing bath temperatures T_{B1} and T_{B_2} two equations are obtained

$$t^2 (T_{B_1} - Tign) = B \qquad \text{(J.24)}$$

$$t^2 (T_{B_2} - Tign) = B \qquad \text{(J.25)}$$

Equating (J.24) and (J.25) gives an equation which can be solved for Tign as follows:

$$t_1^2 (T_{B_1} - Tign) = t_2^2 (T_{B_2} - Tign)$$

$$Tign = \frac{t_1^2 T_{B_1} - t_2^2 T_{B_2}}{(t_1^2 - t_2^2)}$$

Using the data from the $BaCrO_4$ - B system cited above Tign can be calculated.

$$Tign = \frac{(25.6)^2 (702) - (35.6)^2 (682)}{(25.6)^2 - (35.6)^2}$$

$$= \frac{(655.36) (702) - (1267.36) (682)}{- 612}$$

$$= \frac{460091 - 864367}{- 612}$$

$$= \frac{-404276}{-612} = 661°$$

In a similar manner

$$Tign = \frac{(35.6)^2 (682) - (39.4)^2 (673)}{(35.6)^2 - (39.4)}$$

$$Tign = 652°C$$

and again Tign - 652°for an average of 655°C. Yet various
laboratories report a spread of some 40°C in Tign determ-
inations on this system.

If a plot is made with these data to get the old
standard 5 sec Tign (see reference (1) and (2)) the value
obtained is approximately 780-790°C which is well over
the value obtained from the modified ignition equation.

If a plot of (SIT min. is made (see reference 2)
the value obtained is ca 645°C and compares very favorably
with the 655°C obtained from the ignition equation.

There is one more application of the ignition equa-
tion which is worth mentioning; namely, ignition sensi-
tivity. Calculating Tign from equation J.23 and noting
that B $(Tign - Tamb)^2 = (Energy factor)^3$.

Calculations made from this equation setting the
energy factor ("E") for black powder as 1.00 are as follows:

	Tign °C	"E"
Black powder	321	1.00
McLain Starter	458	0.36
B - PbO_2-viton	300	0.61
B - $BaCrO_4$	655	23.6

Earlier experimental work by McLain and Frahm[22]
had shown that McLain Starter was more sensitive to igni-
tion spark than black powder although its ignition temperature
is considerably higher than that of black powder.

As stated previously Equation (J.12) with its various
modifications is not the complete answer to the ignition
problem. It needs amplification and amendment in order
to make it more general and more precise. Price et al[23]
have published a review of "Theory of Ignition of Solid
Propellants" in which they concluded that, "while possess-
ing certain drastic simplifications in common, the vari-
ous quantitative models differ so conspicuously in their
assumptions regarding external initiating stimulus as
to make quantitative comparisons or tests of validity
impossible." These authors did not proceed to make any
constructive suggestions as to further refinement.

These same criticisms can be levelled against the
ignition equat· contained herein although even in its
present rudime ry state it is very useful in systems
design. Perhaps it can be made more useful with some
refinement and additions.

Firstly, it seems quite obvious to us as it has
to others before (Appendix C, reference 26) that ignita-
bility must be intimately related to the energy of acti-
vation of the system.

Secondly, and not so obvious, but we believe to
be important, is the role of burning rate in the theory .
of ignition. Ignition by definition requires that a
substance must be started to combust and started well
enough to continue to combust. Therefore, after the out-
side heat source is expended, the reaction must supply the
necessary heat energy at a fast enough rate to conduct
down the tube and activate the subsidiary layers of the
mix. This heat energy is dependent upon the ΔH of the
reaction and its rate of burning. Its rate of burning
is dependent upon its energy of activation, its coeffi-
cient of thermal transfer and its ΔH of reaction.

The importance of these two additions to the theory
will need much further study but at least the qualitative
effect of them can be discussed.

Returning to equation (J.8)

$$\frac{\partial x}{\partial t} = \frac{K}{\rho C x} \quad (J.8)$$

which states that the rate of burning of the composition
is directly proportional to the diffusivity ($\alpha = K/\rho c$)
and inversely proportional to the distance (x) from the
heat source, this equation should be modified to include
the heat of reaction of the composition and its energy of
activation and read something like the following:

$$\frac{\partial x}{\partial t} = \frac{K}{\rho C x} \cdot \frac{\Delta H_{reaction}}{E_a} \quad (W1)$$

Integration of (W1) between limits x_0 to x and t_0 to t
where $x >> x_0$ and $t >> t_0$ produces

$$x^2 \cong 2\frac{K}{\rho C} \cdot \frac{\Delta H}{E_a} t \quad (W2)$$

substituting $\alpha = K/\rho c$ in $(W2)$ gives

$$x^2 \cong 2\alpha \frac{\Delta H}{E_a} t \quad (W3)$$

- 46 -

Substitution of the value of X^2 from (W.3) into (J.5) yields

$$q_{in} = \frac{KA\left(T_{ign} - T_a\right)}{\sqrt{\pi \alpha \, t \, e^{\Delta H/E_a}}} \qquad (W.4)$$

Solving (W.4) for t (the time to ignite) from a constant heat flow (qin.) gives:

$$t = \frac{K^2 A^2 \left(T_{ign} - T_a\right)}{\pi \alpha \, e^{\Delta H/E_a} \, q_{in}^2}$$

and remembering that $\alpha = K/\rho C$ then

$$t = \frac{K \rho C A^2 \left(T_{ign} - T_a\right)}{\pi \, q_{in}^2 \, e^{\Delta H/E_a}}$$

Some justification for equation W.1 and an explanation of the assumptions made must be given.

First of all $\left(\dfrac{\partial x}{\partial t}\right)$ which is the rate of burning is certainly proportional to the heat of reaction. (See references 32, 33 and 34). Secondly, the rate of burning must be inversely proportional to Ea (the energy of activation) from kinetic theory.

Justification of the use of this functionality is not too clear. However, the following can be said. Use of the $\Delta H/E_a$ fraction has some advantages:

(1) Dimensionless calories $\div$ calories

(2) Mass independent in that both Ea and ΔH are in units of energy per mole.

(3) There is an intuitive objection to the use of a fraction such as $\Delta H/E_a$ because the rate of the reaction very definitely depends upon the Ea in a logarithmic manner. Whether this is also true of the ΔH or not remains to be seen.

Spice and Staveley (Reference 32) give the
modified Maillard and the Chatelier rate
equation for exothermic reactions as $V = \dfrac{kq}{bc^a \rho (T_1 - T_0)}$ (S.1)
where

V = rate of burning in cm sec^{-1} c = specific heat

k = thermal transfer coefficient ρ = density

q = heat or reaction T_1 = burning temperature

b = reaction zone width   To = ambient temperature

which certainly shows the influence of ΔH on the rate. Al-
so, Cottrell and Hill (reference 33) have obtained excel-
lent results with this same equation. Nakahara (reference
34) has also used the ΔH but he has so many constants in
his equation it is difficult to analyze for the function-
ality.

There is some room for questioning the integration
of equation J.8 $\dfrac{\partial x}{\partial t} = \dfrac{K}{\rho c x}$ or $\dfrac{\partial x}{\partial t} = \dfrac{\alpha}{x}$.

$\partial x / \partial t$ is clearly the rate of burning but is x the same
x as in $\partial x / \partial t$? The equation states that the rate of
burning is inversely propostional to a linear distance
called a burning zone, and as a test of this equation some
data was substituted into the equation and the burning zone
width did come out to a few millimeters.

Furthermore, Spice and Staveley's rate equation,
(S-1 above) shows very plainly that Ti is a "predominant
factor in determining the rate of burning." The converse
is certainly also true; rate of burning plays a prominent
role in the determination of the Ti.

In fact an interesting substitution of equation S-1
can be made in J.12.

$$t = \frac{K \rho C A^2 (T_{ign} - T_a)^2}{\pi e q_m^2} \quad (J.12)$$

but from S-1 $\quad (T_{ign} - T_a)^2 = \left(\dfrac{k}{b} \dfrac{\Delta H}{C^2 \rho V} \right)^2$

therefore
$$t = \frac{K \rho C A^2}{\pi e q_{in}^2} \left(\frac{K (\Delta H)}{b c^2 \rho v} \right)^2 \quad (w.7)$$

and
$$t = \frac{K^3 A^2 (\Delta H)^2}{\pi e q_{in}^2 b^2 C^3 \rho v^2} \quad (w.8)$$

which introduces the ∆H or heat of reaction of the system to the time for ignition equation.

However, if the assumption is made that qin, (the heat input of eq. J-10) is the ∆H of reaction during propagation another interesting manipulation can be performed

from S-1
$$\Delta H = b C^2 \rho \left(T_{ign} - T_a \right) V$$

from J-10
$$q_{in} = \frac{K_a \left(T_{ign} - T_a \right)}{\sqrt{\pi e \alpha t}} \quad \text{AND IF } \Delta H \geqq q_{IN} \text{ DURING PROPAGATION}$$

then
$$b C^2 \rho \left(T_{ign} - T_a \right) V = \frac{K A \left(T_{ign} - T_a \right)}{\sqrt{\pi e \alpha t}}$$

solving for t yields
$$t = \frac{K A^2}{\pi b^2 C^3 \rho v^2 e}$$

Although the preceding theory has been developed for application to ignition times and temperatures for pyrotechnic reactions with particular attention given to the role of the rate of burning to these important

parameters, we should point out that much of the ignition
theory can be applied to the interesting problem of rates
of burning. The problem is much too complex to be dis-
cussed in detail in this report. However, one derivation
should be given which we hope may stimulate some further
work along these lines.

Using the Spice and Staveley velocity equation,

$$V = \frac{\Delta H}{b\,c^2\,\rho\,(T_{ign} - T_a)}$$

and J-10
$$q_{in} = \frac{KA\,(T_{ign} - T_a)}{\sqrt{\pi\,e\,\alpha\,t}}$$
and assuming

as before that qin in J-10 is just the ΔH of continuing
reignition for successful propagation, then;

$$V = \left[\frac{KA\,(T_{ign} - T_a)}{\sqrt{\pi\,e\,\alpha\,t}}\right]\left[\frac{1}{b\,c^2\,\rho\,(T_{ign} - T_a)}\right]$$

$$= \frac{KA}{(\sqrt{\pi\,e\,\alpha\,t})(b\,c^2\,\rho)} \qquad (W.10)$$

and
$$V^2 = \frac{K^2 A^2}{(\pi\,e\,\alpha\,t)(b^2\,c^4\,\rho^2)} \qquad \text{but } \alpha = \frac{K\,\rho}{c}$$

therefore
$$V^2 = \frac{K A^2}{\pi\,e\,t\,b^2\,c^3\,\rho^3} \qquad (W.11)$$

Using the $\frac{\Delta H}{Ea}$ concept
$$V^2 = \frac{K A^2}{\pi\,b^2\,t\,c^3\,\rho^3}\,e^{\Delta H/Ea} \qquad (W.12)$$

This equation compares somewhat with other treatments of the theory of rate of burning, particularly that of Hill, Sutton, Temple and White[35] derived by integrating the following equation:

$$V_g \rho \frac{de}{\partial x} + k \frac{d^2 T}{dx^2} - V \rho c \frac{dT}{dx} = 0 \quad (H.1)$$

Equation (H-1) expressed the balance, in a thin section, of heat generated by reaction, heat gain or loss by conduction and heat loss by material movement relative to the reaction zone where V is the rate of
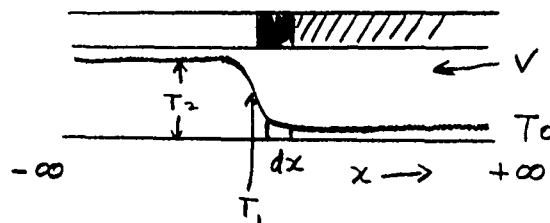
propagation, x the linear coordinate, q the heat of reaction per gram, and ρ the density of unburnt material, e the fraction reacted of the component not in excess, k the thermal conductivity, T the temperature and c the specific heat of the unburnt material At To (initial temperature) there is no reaction thus:

$$V_g \rho e + k \frac{dT}{dx} - V \rho c (T - T_0) = 0 \quad H.2$$

This equation can be solved only if:

(1) T is a known function of x.

(2) e is a known function of x

(3) $\frac{de}{dt}$ is a known function of e and T.

Procedure (3) has been followed by Bell[36] who assumed zero or first order kinetics and by Boys and Corner[37] who assumed first or second order kinetics.

If first order is assumed ($\frac{de}{dt}$ = B (1 - e) exp $-\frac{Ea}{RT}$

then

$$V^2 = \frac{\left[\frac{k B}{c \rho} e^{-Ea/RT_2} \right]}{\left[\frac{Ea (T_2 - T_0)}{R T_2^2} - 1 \right]} \quad (H.3)$$

- 51 -

where T_2 is the final temperature, Ea = activation energy and B is another parameter.

An earlier and less general treatment is based on the assumption that there is an ignition temperature Ti below which $\frac{de}{dt}$ and e are negligible and equation H-2 gives

$$V = \frac{k}{\rho c} \left(\frac{1}{T'-T_0} \right) \left(\frac{\partial T}{\partial x} \right)_{T'} \quad (H.4)$$

wherein T' is any temperature below Ti. Also since $V = \frac{dx}{dt}$

$$V^2 = \frac{k}{\rho c} \left(\frac{1}{T'-T_0} \right) \left(\frac{\partial T}{\partial t} \right)_{T'} \quad (H.5)$$

Maillard and LeChatelier made the further assumption: that $\frac{dT}{dx} = \frac{(T_2 - T_1)}{\Delta x}$ where T_2 is the maximum temperature and Δx is the width of the reaction zone.

Equation H-5 then becomes

$$V^2 = \frac{k}{\rho c} \left(\frac{T_2 - T_1}{T_1 - T_0} \right) \left(\frac{1}{\Delta T} \right) \text{ where } \Delta T \text{ is}$$

the "time width" of the reaction zone and is equal to the time to ignition from one layer to another.

The t term in equation (J.11) which is

$$t = \frac{k^2 A^2 \left(T_{ign} - T_a \right)^2}{\pi e \alpha q_m^2} \quad (J.11)$$

can be replaced by its value from H-6 and the following equation is obtained.

$$\frac{\alpha}{V^2} \left(\frac{T_2 - T_1}{T_1 - T_0} \right) = \frac{k^2 A^2 \left(T_{ign} - T_a \right)^2}{\pi e \alpha q_m^2} \quad H.7$$

- 52 -

Writing T Max for T_2, Tign for T_1 and Ta for T_0 and rearranging yields

$$V^2 = \frac{\pi \alpha^2 e\, q_{in}^2 \left(\dfrac{T_{max} - T_{ign}}{T_{ign} - T_a}\right)}{K^2 A^2 \left(T_{ign} - T_a\right)^2} \quad (H.8)$$

but $\alpha^2 = \dfrac{K^2}{\rho^2 c^2}$ and finally

$$V^2 = \frac{\pi e\, q_{in}^2 \left(T_{max} - T_{ign}\right)}{\rho^2 c^2 A^2 \left(T_{ign} - T_a\right)^3}$$

therefore

$$V = \frac{\Delta H \sqrt{\pi e}\, \left(T_{max} - T_{ign}\right)^{1/2}}{\rho c A \left(T_{ign} - T_a\right)^{3/2}}$$

F. Defects

The experimental work on the determination of the effect of defects on the reactivity of the $KClO_3$ - S system as well as the PbO - Si system was performed during the first two years of this grant and is to be found in references (1) and (2).

However, inasmuch as this is a final report, a brief summary of the results obtained is provided as follows:

1. Inherent Defects

    A. Crystallization conditions of $KClO_3$

        (1) Congo Red solution
        (2) "Dreft" solution
        (3) $KMnO_4$ solution

All of these showed that the crystal structure of the $KClO_3$ was important to the reaction rates and temperature of the preignition reaction.

2. Doping

    A. $KClO_3$

Doping of $KClO_3$ with $Cu(ClO_3)_2$ resulted in massive changes in the reactivity of the system as evidenced

by DTA and ignition experiments. $AgClO_3$ doping gave considerable effect as well.

B. Sulfur

Doping of sulfur with lead (PbS) resulted in minor changes in reactivity of the system.

3. Burning Rate Studies

A great deal of experimental time in the first two years of this grant was spent in trying to determine the effect of defects on burning rate of the fuel composition ($KClO_3$-S-$NaHCO_3$) the results of which are reported in references (1) and (2).

In summarizing these results it can be said that no pronounced changes were found. These negative results can be explained in part by the wide variation experienced in burning rates even with the same samples which would obscure the effects found by more sensitive methods.

For further discussion of these results see this report page 56.

G. Mechanical Activation and Thermal Treatment

Freshly ground and mixed samples of sulfur and $KClO_3$ gave lower ignition temperatures and sharper P.I.R. slopes than those stored after mixing at 65°C.[1]

Figures 23, in reference (2) showed that there were pronounced differences in the behavior of $KClO_3$-S mixes with varying storage and mixing procedures. These differences made themselves evident on DTA traces by differences in the temperature of the onset of the P.I.R., as well as considerable difference in the shape of the exotherm.

Attempts to determine effects of grinding and heated storage on the $KClO_3$-S-$NaHCO_3$ by means of burning rate measurements were unsuccessful. However, burning rate measurements on the PbO-Si system were able to show a 20% increase in rate of the ground PbO over the unground. The reasons for the lack of success in measuring mechanical and thermal treatment effects by burning rates for the $KClO_3$-S-$NaHCO_3$ system is believed to be due to the wide variation in burning pressures in the small tubes used in this investigation and is explained in more detail in the following. See Section IV, H below.

H. Confinement

The influence of K factor (ratio of burning surface to nozzle area) on the burning rate of pressure-sensitive mixes was discussed in reference (2).

Since that time some quantitative data have been received on the influence of pressure on $KClO_3$-S type mixes, which is summarized below.[38]

Strand burnings in the Crawford bomb showed that the $KClO_3$ based fuel-agent mixes obey the familiar solid propellant burning rate expression $r = Cp^n$ where r = rate of burning in inches/sec., C is a constant and equal to 3.9×10^{-3}, and $n = 0.55$ for this formulation. Rates of burning at various pressures are shown below.

Pressure in atmospheres	Rate of Burning (in sec)
1	0.018
3	0.035
10	0.060

It was also found that the burning temperature of the mix increases with the ambient pressure in an exponential manner.

These data explain the detonations that occurred in the burning rate experiments performed and reported in reference (2) inasmuch as the slag formed during the burning sometimes caused a large increase in K factor and thus a large increase in rate of burning and pressure which led to a runaway reaction.

V. DISCUSSION

A. Hedvall Effect and Tammann Temperature

1. A very important application of the Hedvall Effect was exemplified by the $KClO_3$-S system. The experimental determinations of ignition temperatures showed very clearly that these temperatures coincided with the liquid phase transition of sulfur (the $\lambda \to \pi$ transition). In fact, it was this finding which led to the reaction mechanism proposed in the first year and confirmed by later work.

2. The role of Tammann temperature was ascertained by thermoconductimetric analysis on the PbO-Si system[2] and on doped potassium chlorates. As can be seen from the data, Cu^{++} doped $KClO_3$ has a melting point of 333°C or 606°K. Its Tammann temperature would therefore be 303°K, 30°C, or 86-88°F. Cu^{++} doped $KClO_3$ should be capable of reacting with sulfur at room temperature which was observed in two experiments and reported in

reference (1).

In this connection it is interesting to note that Freeman and Rudloff have observed that both Cu^{++} and Fe^{+++} doped $KClO_3$ react at room temperatures.[39]

B. Thermoconductimetric Analysis

One of the primary goals of the grant was realized when a cell was designed and built which could be used for high temperature (Ca 500°C) conductivity measurements. This cell gave reproducible results and proved itself on several systems to be more sensitive in discerning of pre-melting ion mobility than any other method. It is our belief that a very useful tool in investigation of solid-solid reaction has been designed and tested.

C. Moisture

The role of moisture in the $KClO_3$-S reaction has been demonstrated to be a very important one. It has been proven that the rate of reaction is a maximum at some low percentage of moisture but exactly what that percentage is cannot be stated at this time.

Baldwin and Wooldridge[38] stated that this reaction "is probably activated by the generation of small amounts of water---which lowers the initiation temperature of the $KClO_3$-S reaction."

All that can be said at present about the effect of moisture is that the reaction when "bone" dry or when quite wet (over 0.5%) reacts more slowly and has a higher temperature of ignition than when a relatively small amount of moisture is present.

D. Ignition and Rates of Burning

A large portion of the effort in the third year was devoted to the derivation of a semi-empirical "Ignition Equation" and its evaluation.

This derivation is a mathematically rigorous one up to the point where the energy of activation and burning rates were included. To our knowledge, this is the first time that this derivation has ever been published in a complete and rigorous form.

An important part of this work was the definition of "ignition temperature" and the proof that the energy of activation and rate of burning must be included in

such a definition. In fact, one of the significant out-growths of the derivation of the ignition equation was that the rate of burning which fell out of this work checked very closely with that of Maillard and LaChatelier as reported by Spice and Staveley[32] and by Cottrell and Hill.[33]

As pointed out in the preceding section, the modified ignition equation has not been evaluated due to lack of time; however, it does show application to:

(1) Difference in energy required to ignite at different temperatures.

(2) Refinement of the data from Henkin-McGill determinations from different laboratories.

(3) Theoretical justification of the minimum spontaneous ignition temperature (S.I.T. min) (See reference 2).

(4) Theoretical assessment of ignition sensitivity, which is quite different than ignition temperature.

After writing the section of this report dealing with ignition theory, we happened upon two pertinent papers[40],[41] which we believed necessary to include. Although the main purpose of (40) was to explain the effect of surface heat release on combusion stability, the approach to their problem was begun with the equation governing heat conduction in the solid phase namely:

$$\frac{\partial T}{\partial t} = \lambda(t) \frac{\partial T}{\partial x} + \kappa \frac{\partial^2 T}{\partial x^2} \qquad (M.1)$$

$$\text{where } \lambda = ae^{-E_a/RT}$$
$$x = \text{linear distance}$$

and all others their usual significance.

The second of these papers,[41] entitled "An Approximate but Complete Model for the Ignition Response of Solid Propellants" was attempting to prove the need for a term in the equation to express the regression of surface of the propellant in the theoretical treatment of ignition. These authors start with the following equation

$$\frac{\partial u}{\partial T} - R_{ex} \frac{\partial u}{\partial x} = \frac{\partial^2 u}{\partial x^2} \qquad (B.1)$$

in which $U = \dfrac{RV}{E}$ = dimensionless solid temperature

$T = \left(\dfrac{Rb}{E\gamma}\right)^2 t$ = dimensionless time

$X = \dfrac{Rb}{Ek}\, \chi$ = dimensionless distance from surface

$R_{ex} = \dfrac{E\rho c}{Rb}\, r$ = dimensionless regression rate

In the above U is absolute temperature, t is time, χ is distance from the surface, r the solid velocity, E/R the activation energy for surface reactions, $\gamma = (K\rho c)^{1/2}$ where k, ρ, c have their usual significance and b is the dimensionless parameter converting surface heat flux, f, to a dimensionless flux F, (F = f/b).

A comparison of equations (M1) and (B1) show that they are virtually the same except that in B1 the coefficient of $\partial u / \partial \chi$ is $-\dfrac{E\rho c}{Rb}$ and in M1 the similar coefficient of $\partial T / \partial \chi$ is ae $^{-E/RT}$. As can be seen both equations contain the concept of activation energy. It is important to note that (B1) also includes the concept of the rate of burning applied to the concept of ignition as was proposed by us on page 46 of this report. Indeed, reference (41) makes the following statement; "Early theories of ignition, describing events leading to a bootstrapping exothermic reaction, cannot be extended to describe the complete ignition process terminating in its steady deflagration. The complete description requires consideration of surface regression." Thus, these authors are saying that a definition of ignition must include steady state combusion and that the rate of burning of the ignited material is important, and they also included a term for the heat flux generated by the chemical reactions at or near the surface.

E. Defects

A large portion of the first year's work was given to modification of the $KClO_3$ crystals either by:

(1) Crystallization from various dye solutions
(2) Crystallization from various detergent solutions
(3) Incorporation of dopants by crystallization

Similar work was done on sulfur but to a much smaller extent.

A spectacular demonstration of increasing the sensitivity of crystals occurred in the first year's work when sulfur mixed with a Cu^{+2} doped $KClO_3$ detonated on standing at room temperature. This was repeated with similar results to confirm our findings.

This is of importance to the industry, inasmuch as it has been standard procedure in pyrotechnic plants to require, bronze, brass or copper, screens and tools.

All future safety manuals, which deal with $KClO_3$ mixes, should specifically state that no copper or copper alloy should be used. Stainless steel should be specified in their stead.

F. Mechanical Activation, Hardness and Thermal Treatment

One of the outgrowths of this research was the finding by McLain and Lewis[1] and confirmation by McLain and McClure[2] that freshly ground and mixed $S-KClO_3$ mixtures gave lower ignition temperatures and sharper preignition reaction slopes than stored mixtures. Annealing tests were carried out by McLain and McClure[2] and it was found that the freshly ground materials could be returned to their less active state by storage above the Tammann temperature.

Activation by grinding of reactants should be affected by hardness characteristics of the materials. Any diffusion controlled reaction, such as solid-solid or liquid-solid, should also be affected by the hardness as such is beyond the scope of this grant, general devotion to the problem of solid state chemistry makes it almost obligatory to mention briefly as an area that deserves further study.

One of the few references to hardness in the current literature is that of Sirdeshmukh (reference 24) who performed microhardness indentation measurements on the following three nitrates; $Pb(NO_3)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$. Contrary to previous expectations based on melting point, solubility, thermal expansion, Gruneisen constant, elastic constants, and Raman intensities, $Ba(NO_3)_2$ was found to be considerably softer than the other two. Yet all three are face centered cubes. It has been an experimental fact

- 59 -

for many years that $Ba(NO_3)_2$ is much more reactive in flare and primer mixes than the other two, but as mentioned, its melting point, etc., should not allow this. The hardness data would account for this remarkable reversal. Perhaps then hardness can be and should be a specification measurement, particularly if some theoretical grounds can be established for the effect of hardness in pyrotechnic reactions. Experience has shown that present specifications for the purchase of chemical ingredients of starter mixtures (MnO_2, Fe_2O_3, PbO_2, $BaCrO_4$, et al) do not insure the correct material for performance in the end item. Some of this problem has been solved by writing a performance specification, but this is not completely satisfactory because the vendor is usually loath to get into the art of primer mixing and because in a two or three component mix it is very difficult to standardize on the other components. It is certain that the reactivity of solid materials is dependent upon the nature and number of defects. If hardness is so dependent, some measure of reactivity can be ascertained.

A brief literature search on hardness was performed. The more important references found by the search are (25) (26) (27) (28) (29). Based upon this search and some fundamental structural analysis, the hardness of crystals was found to be dependent upon the following:

     1. Lattice energy
       a. crystal habit
       b. ionic charge

     2. Cationic and anionic field strength

     3. Extent and type of defects

     4. Radius ratio

     5. Size of the microcrystals making up the macro-mosaic and the extent of departure from perfect alignment.

These are not listed in order of importance and indeed, numbers 3 and 5 are not readily measureable with any real degree of certainty. It was found, however, in this survey that to a first approximation the hardness of members of a homologous series was affected in a predictable manner by their radius ratio.

It was also found that micro-indentation hardness testing, by means of a Tukon tester or equivalent, gives

reproducible and meaningful values and shows great promise as another measurement of value in predicting solid state reactivity. Hardness measurements should be of particular importance in the determination of physical effects of doping and the choice of suitable dopants based upon ionic radius data.

In an attempt to anneal out strains induced by grinding, the $KClO_3$ was subjected to varied temperature conditions after grinding. The results were not very conclusive in that annealing did not show stabilization; however, freshly ground material was always more reactive than unground or ground material which was stored for a month or two.

G. Rates of Burning and Confinement

Considerable effort was spent on attempts to measure the effect of various additives, dopants and other modifications of $KClO_3$ and sulfur on the rate of burning of the fuel mix ($KClO_3$-S-$NaHCO_3$).

We were forced to conclude at the end of the second year and after several detonations while burning this mix during experimental runs that this method was not sufficiently sensitive to these variables but <u>was</u> exceedingly sensitive to pressure variation. See reference 38 for confirmation of these findings.

The reason for the detonations, beyond any doubt, was the effect of a variable K factor during burning. Thus, as burning progressed down the tube, slag formation made the throat area smaller which increased the pressure causing more mix to burn at a faster rate and this happened progressively until detonation resulted.

It was pointed out that this same condition can occur during the pressing operation at a loading plant and under such conditions would not be merely a fire or rapid combustion but would be a detonation and very hazardous to the personnel operating the press.

VI. Conclusions

The following conclusions can be drawn from the results of the three years of study.

A. The mechanism of the $KClO_3$-S reaction is independent of the decomposition of the $KClO_3$. It is, however,

dependent upon the lattice "looseness" of the $KClO_3$ and its permeability to the sulfur molecules. Untreated $KClO_3$ reaches the required looseness at the temperature at which sulfur undergoes a liquid-liquid phase transition.

B. Copper and copper alloy tools and screens should be removed from $KClO_3$ operations as a safety measure.

C. Thermoconductimetric measurements are of real value in the study of reactivity of solids.

D. Burning rate measurements are of little value in the study of reactivity of this system.

E. The previous treatment of the constituents (notably $KClO_3$) such as mechanical and thermal treatment, and defects of all types play a measurably important role in the stability of the system.

F. The moisture content of the system is extremely important. The rate of the $KClO_3$-S reaction is a maximum at some low percentage of moisture ($0.5 \pm 0.3\%$).

G. The hardness of crystalline solids should be studied further to serve as an indicator of reactivity.

H. The growth of burning to detonation of fuel mix ($KClO_3$-S-$NaHCO_3$) is profoundly enhanced by a large K factor in the munition.

VII. LITERATURE CITED

1. J. H. McLain and D.V. Lewis, "Effect of Phase Change in Solid-Solid Reactions", WCDC 6465, Grant DA-AMC-19-035-77(A), Jan. 1966.

2. J. H. McLain and M.D. McClure, "Effect of Phase Change in Solid-Solid Reactions, "WCDC 6566, Grant DA-AMC-18-035-77(A), Nov. 1966.

3. J.A. Hedvall, "Solid State Chemistry; Whence, Where and Whether", Elsevier Publishing Company, Amsterdam/London/New York 1966.

4. G. Tammann, Z. Anorg. Allgem. Chem $\underline{149}$ 31 (1925).

5. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry".

6. M. Nagatani and T. Seiyama, "Effects of Moisture and Thermal Cycling on the Phase Transitions of Ammonium Nitrate", Kogyo Kagaku Zasshi, $\underline{67}$ 2010-14 (1964).

7. William Ripley, Pvt. Communication.

9. J.A. Hedvall and S.O. Sandberg, Z. Anorg. U. Allg. Chemie; $\underline{240}$, 15, (1938).

10. M.J. Pryor and U.R. Evans, J.C.S. 181 (1949).

11. Eli S. Freeman and D.A. Anderson, Nature 140 (1962).

12. J. Rose, "Dynamic Physical Chemistry", John Wiley and Sons, N. Y. (1961).

13. H. Henkin and R. McGill, Ind and Eng. Chem $\underline{44}$ 1391 (1952).

14. Garner and Haycock, Proc, Roy, Soc. $\underline{A211}$, 335, (1952).

15. Jen Chiu, "A New Approach to Electrical Thermal Analysis", Abstract of a paper presented at the Fourth Thermal Analysis Institute, Fairleigh-Dickinson University, June 21-23 (1965).

16. L.G. Berg and N.P. Burmistrova. Russ. J. Inorg. Chem. (Eng. Translation) $\underline{6}$ 996 (1961).

17. E.S. Freeman and W. Rudloff, 2nd Quarterly Progress Report No. U6054-6 Contract DAAA15-67-C-0119, August 1967.

18. D.M. Johnson, "Ignition Theory: Application to the Design of New Ignition Systems", RDTR No. 56, 24 Nov. 1965. U.S. Naval Ammunition Depot, Crane, Indiana.

19. Rideal and Robertson, P.R.S. A195, 135 (1948).

20. Copp, Napier, Nash, Powell, Skelly, Ubbelohde and Woodward, Phil. Trans. Series A, No. 831, Vol. 241, pp. 197-296.

21. Kirk-Othmer, Vol. 8, Explosives.

23. Price, E.W., Bradley H.H., Jr., Dehority, G.L. and Ibiricu, M.M., "Theory of Ignition of Solid Propellants" NAVWEPS Report, 8987 NOTS TP 3954, U.S. Naval Ord. Test Station, China Lake, California, March 1966.

24. D. Sirdeshmukh, J. Phys. and Chem. Solids, 27, 1557-58, (1966).

25. J.N. Plendl and P.J. Gielisse, Phys. Rev. 125, 829 (1962).

26. B.W. Mott, "Micro-indentation Hardness Testing", Butterworths, London, 1956.

27. K. Fajans, Zeit, Krist, 61 (1925).

28. H.V. Wartenberg, Z., Elektrochem. 27 (1921).

29. R.R. Jones, Educ. in Chem. 2, 69 (1965).

30. G.A. Marxman and C.E. Wooldridge, "The Effect of Surface Reactions on the Solid Propellant Response Function", ICRPG/AIAA 2nd Solid Propulsion Conference, Anaheim, California, June 6-8, 1967, p. 66-74.

31. A.D. Baer and N.W. Ryan, Ibid., p. 128-35.

32. Spice, J.E. and Staveley, L.A.K., J.S.C. I, 58, 348 (1949).

33. Cottrell, T.L. and Hill, R.A.W., 4th Symposium on Combustion (International). Williams and Wilkins, Baltimore, Md., pp. 349-52 (1953).

34. Nakahara, S.; J. Ind. Explos. Soc, Japan 21, 363-74 (196).

35. R.A.W. Hill, L.E. Sutton, R.B. Temple and A. White, Research Supplement, 3-12 569, (1951).

36. R.P. Bell, Private communication.

37. Boys, S.F. and Corner, J. P.R.S. A197, 90 (1949).

38. Baldwin, J.E. and Wooldridge, E.E., "Pyrotechnic Dissemination Research Studies", SRI Project PAU-4900, Contract DA-18-035-AMC-122(A), Stanford Research Institute, Menlo Park, California.

39. Freeman, E.S. and Rudloff, W. Third Quarterly Progress Report, No. U6054-9, Contract No. DAA15-67-C-0119. IIT Research Institute, Chicago, Ill.

40. Marxman, G.A. and Wooldridge, E.E. "The Effect of Surface Reactions on the Solid Propellant Response Function", ICRPG/AIAA, 2nd Solid Propulsion Conference, Anaheim, California, June 6-8, 1967, pp. 66-74.

41. Baer, A.D. and Ryan, N.W., Ibid., pp. 128-35.

APPENDIXES

APPENDIX A

Thermoconductimetric Analysis
NiSO₄·7H₂O

Figura A-1

Figure A-2

PbO-Si System.

Appendix 1

$1/T \times 10^3$
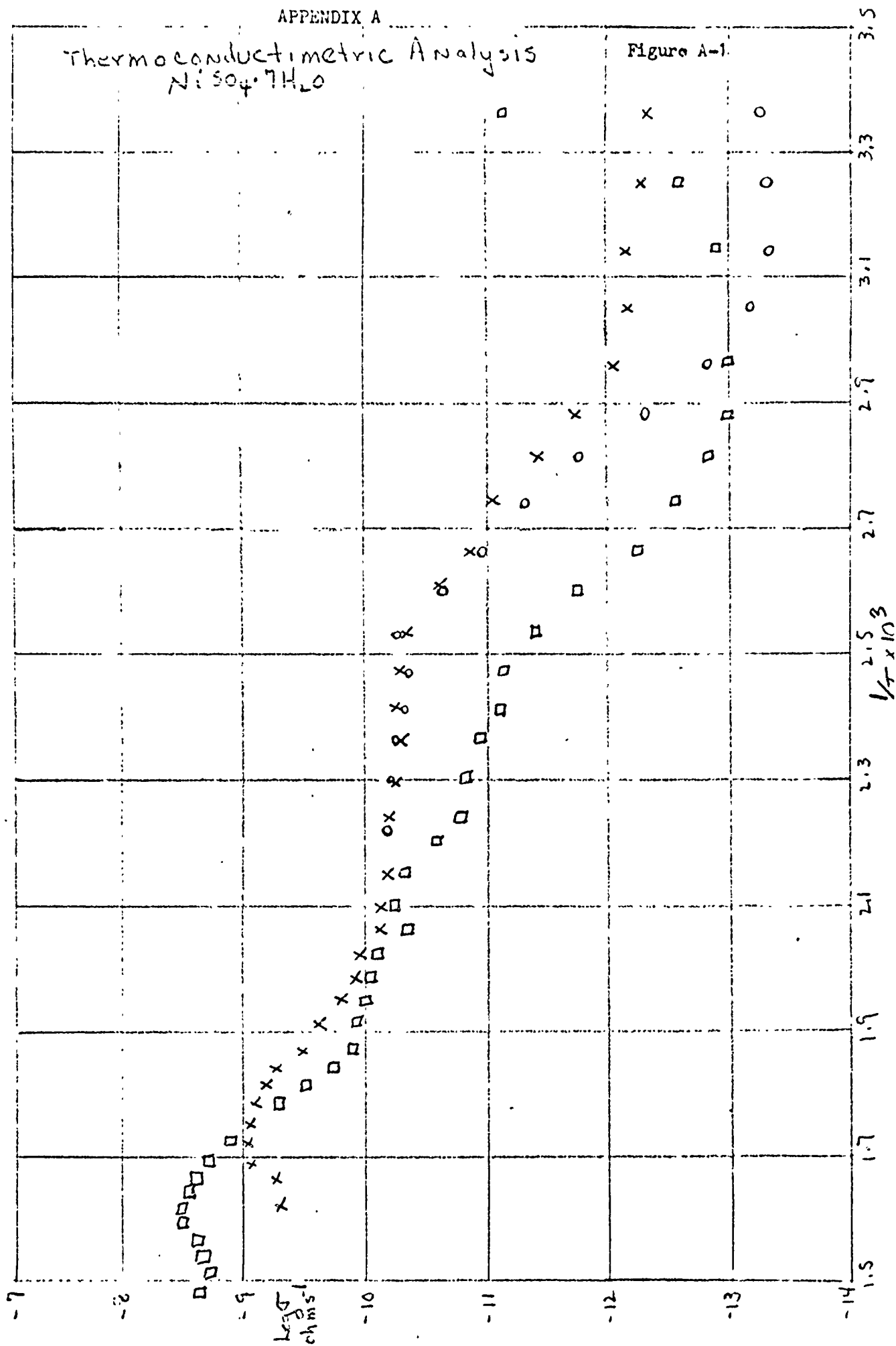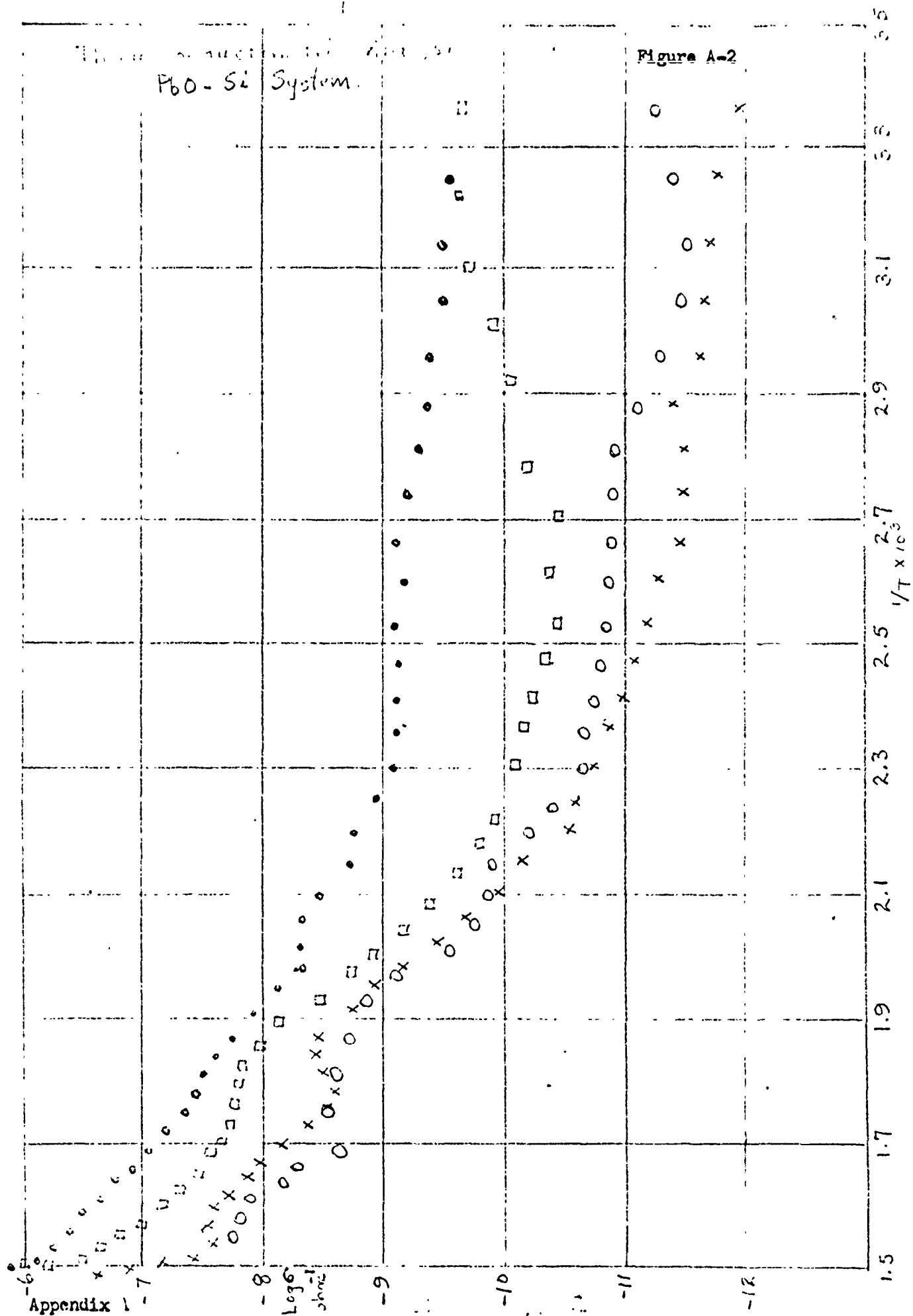
CONDUCTIVITY Cell MODIFICATIONS
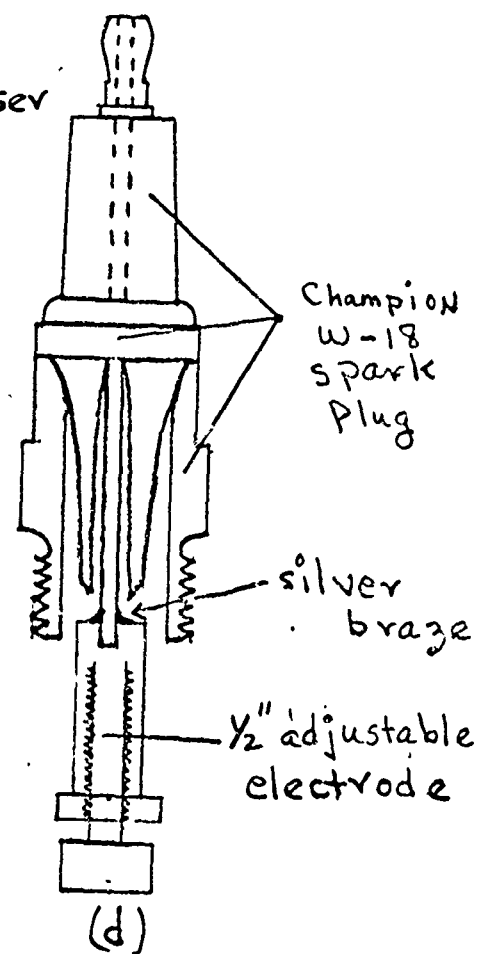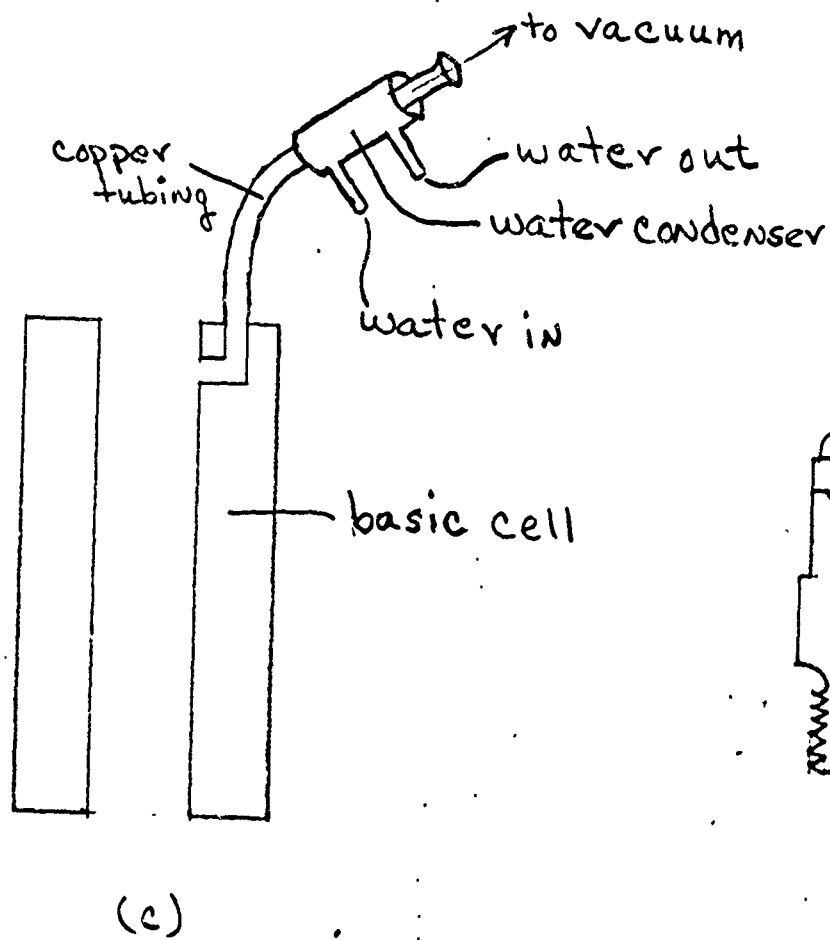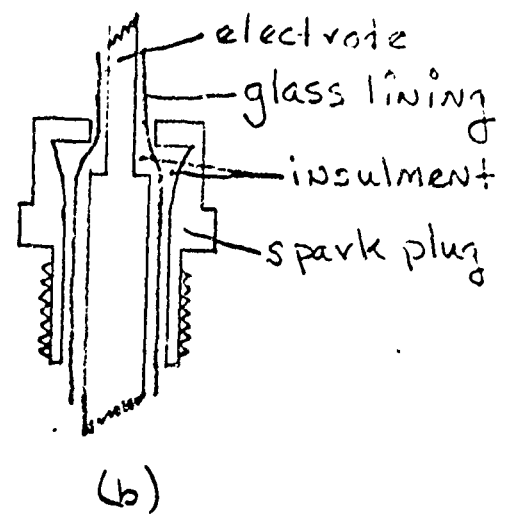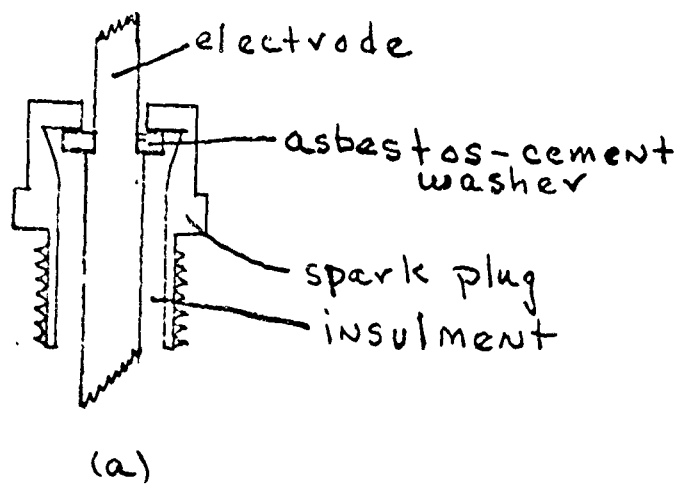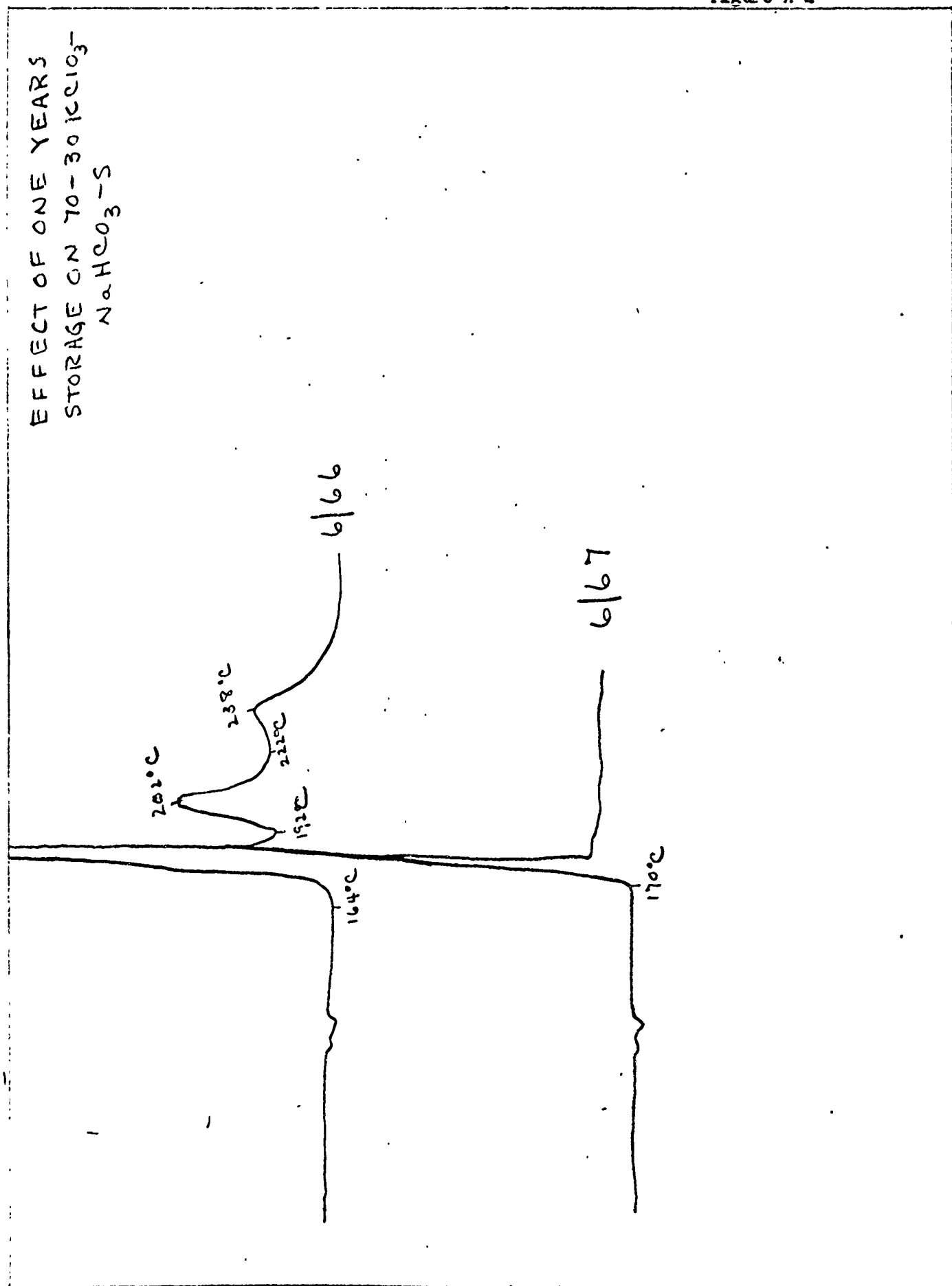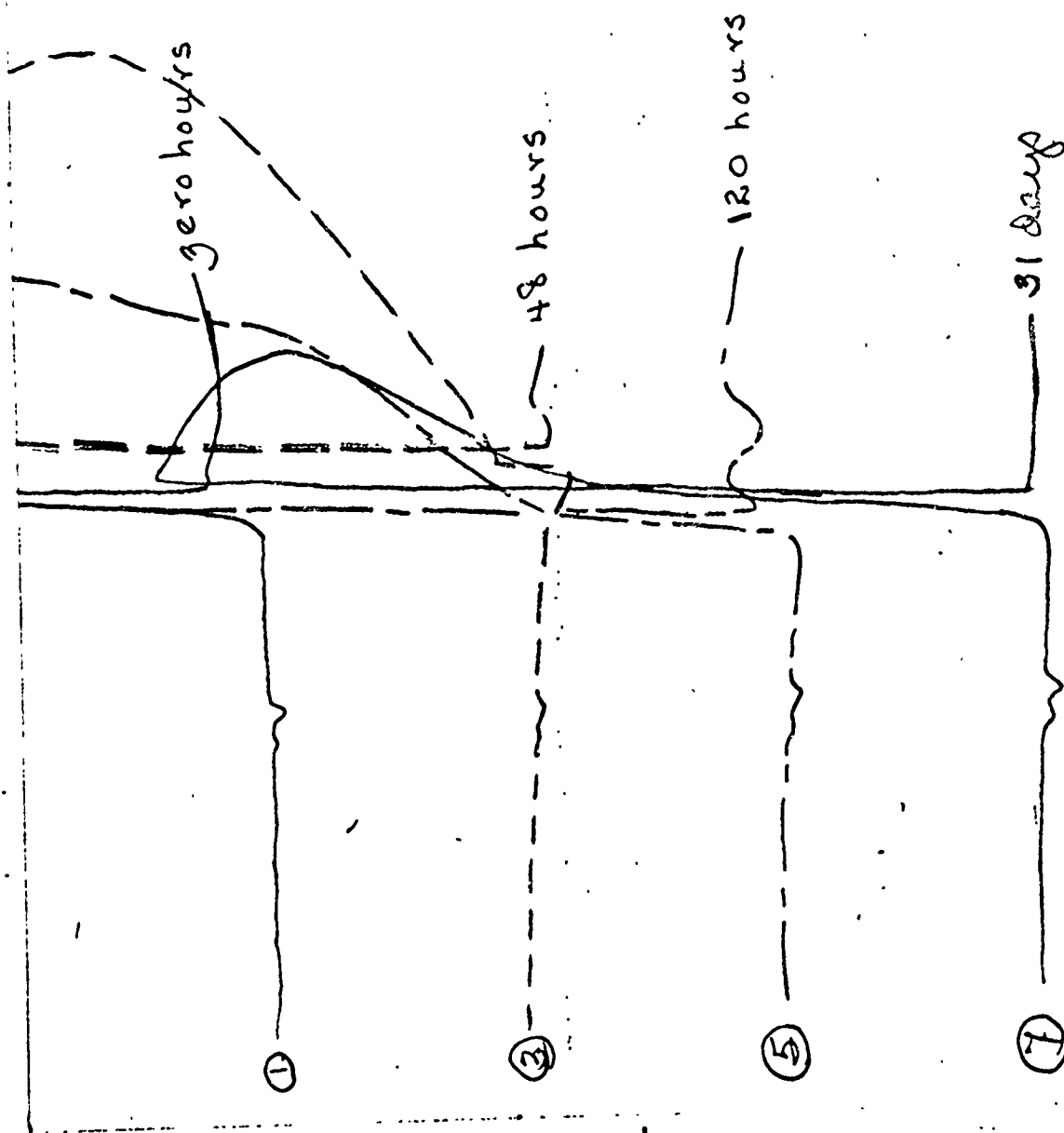
(a)

electrode
asbestos-cement washer
spark plug
insulment

(b)

electrode
glass lining
insulment
spark plug

(c)

to vacuum
copper tubing
water out
water condenser
water in
basic cell

(d)

Champion W-18 spark plug
silver braze
½" adjustable electrode

Figure A-4

EFFECT OF ONE YEARS
STORAGE ON 70-30 KClO$_3$-
NaHCO$_3$-S

6/66

238°C

211°C

202°C

191°C

6/67

164°C

170°C

ΔT

T,°C

Appendix A

EFFECT OF STORAGE AT 6% R.H.
ON
70-30 FUEL MIX

zero hours

48 hours

120 hours

31 days

ΔT

T, °C

① ③ ⑤ ⑦

Appendix A

EFFECT OF STORAGE AT 87% RH
ON
70-30 FUEL MIX

24 hours

72 hours

15 days

2

4

6

T, °C

ΔT

EFFECT OF STORAGE AT 3.27%RH ON 70-30 FUEL MIX
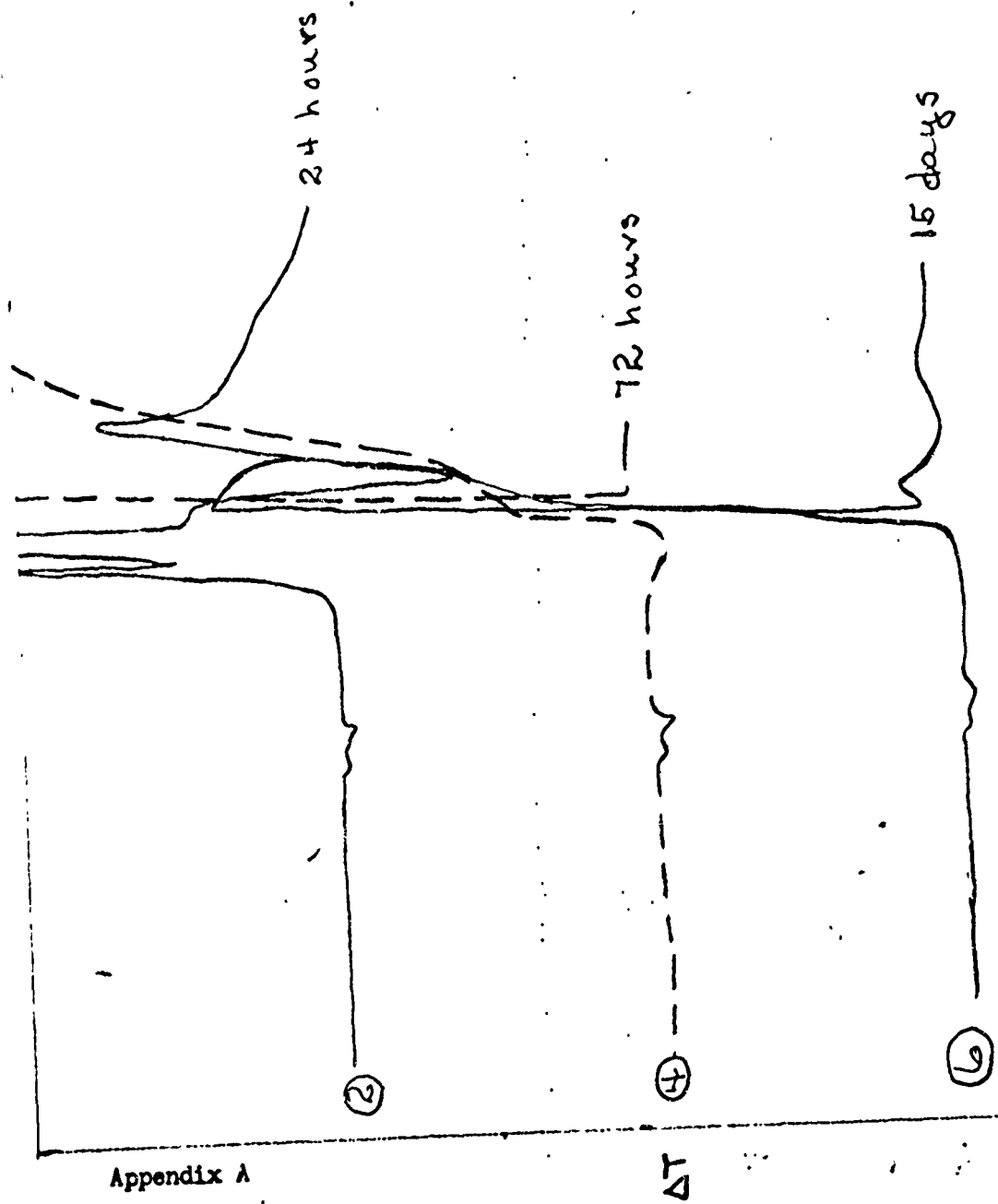
Figure A-7
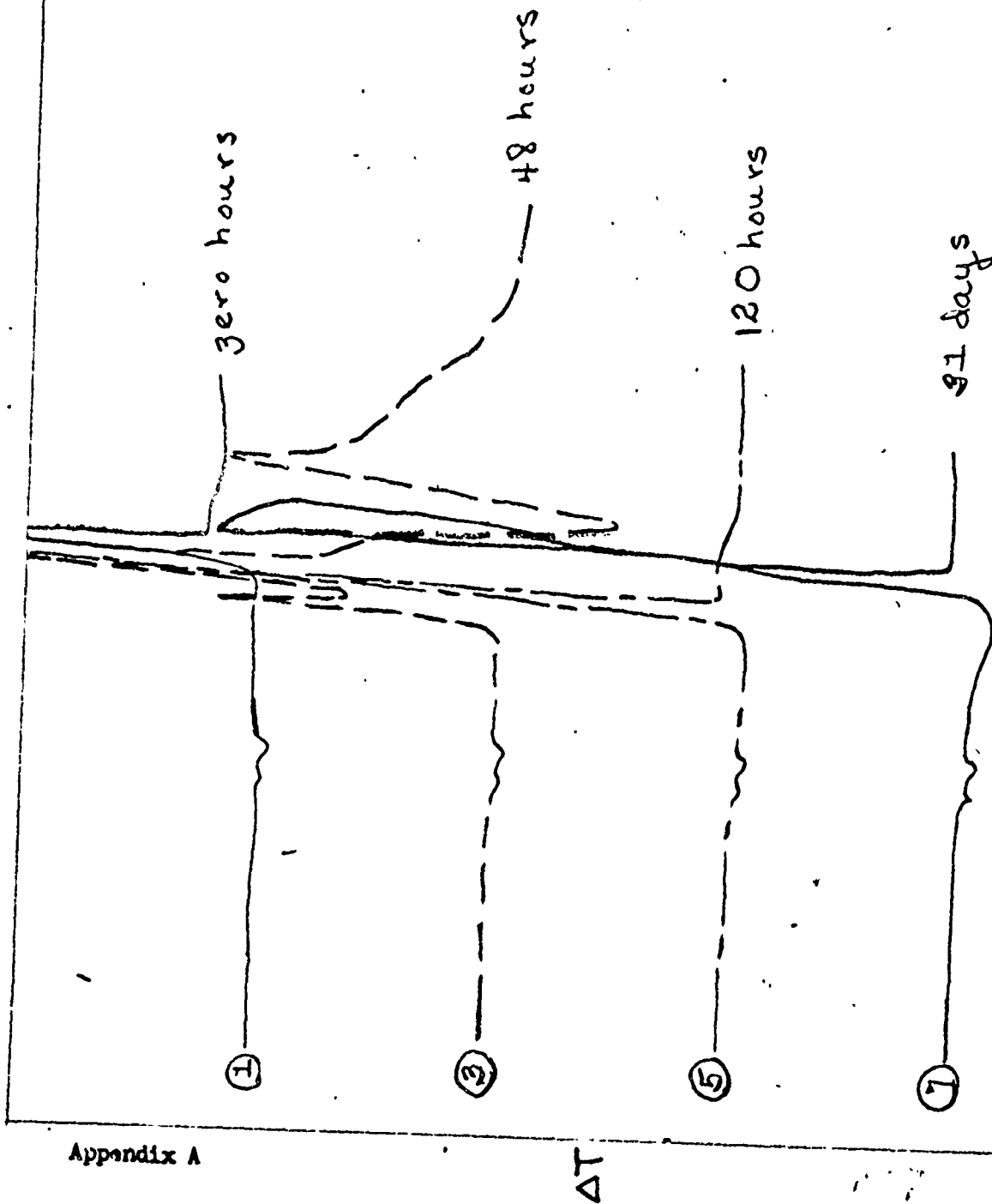
Appendix A

Figure A-8

EFFECT OF STORAGE AT 3.2% R.H.
ON
70-30 FUEL MIX

24 hours

72 hours

15 days

T, °C

ΔT

② ④ ⑥
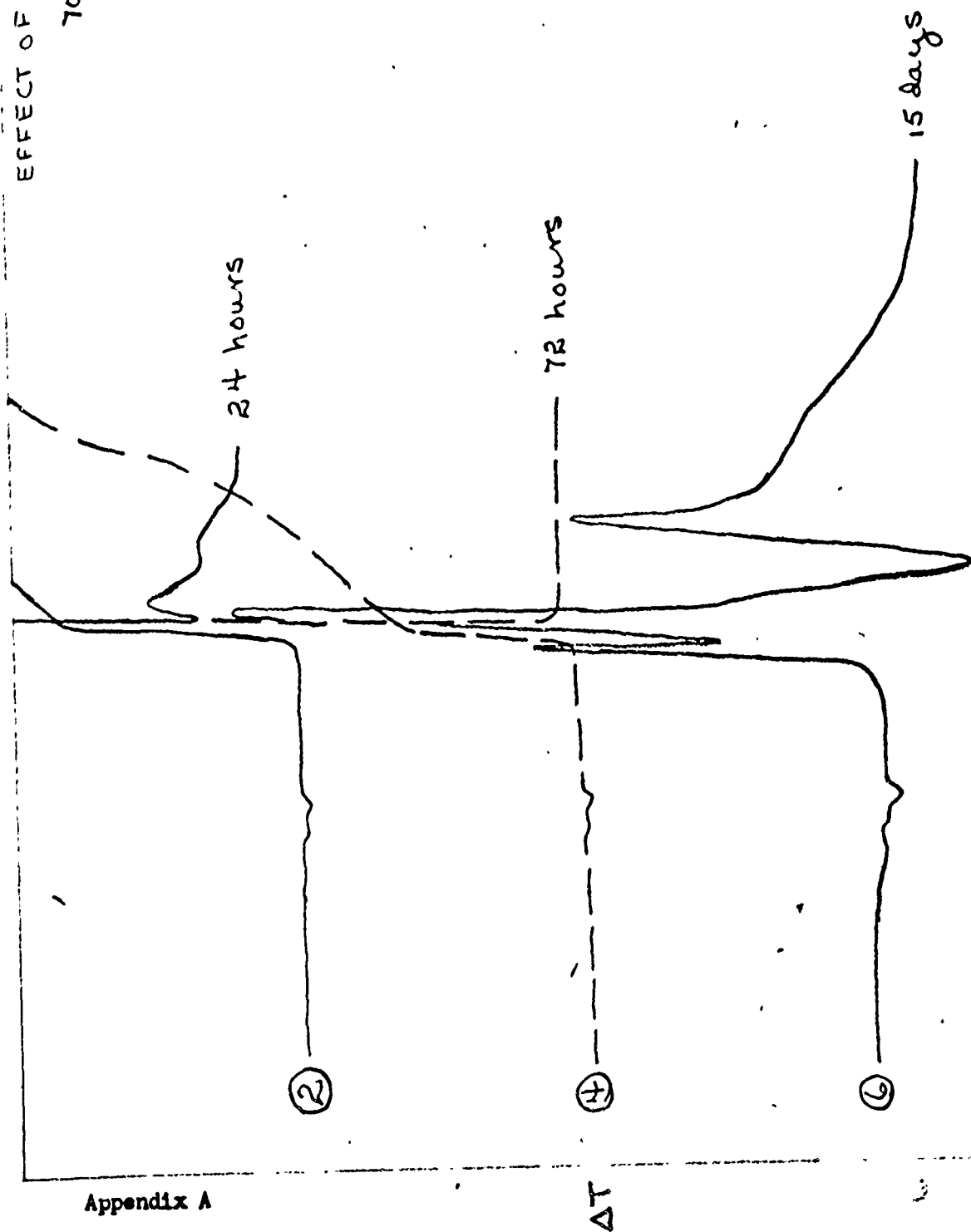
Appendix A

EFFECT OF STORAGE AT 2.5% R.H.
on
70-30 FUEL MIX

Zero hours

48 hours

120 hours

31 days

① ③ ⑤ ⑦

ΔT

T,°C

Appendix A

EFFECT OF STORAGE AT 8.5 % R.H.
ON
70-30 FUEL MIX

2+ hours

72 hours

15 days

T, °C

②

⊕

6

ΔT

EFFECT OF STORAGE AT 47.2% R.H.
ON
90-30 FUEL MIX

① zero hours

② 48 hours

⑤ 120 hours

⑦ 31 days

ΔT

T, °C
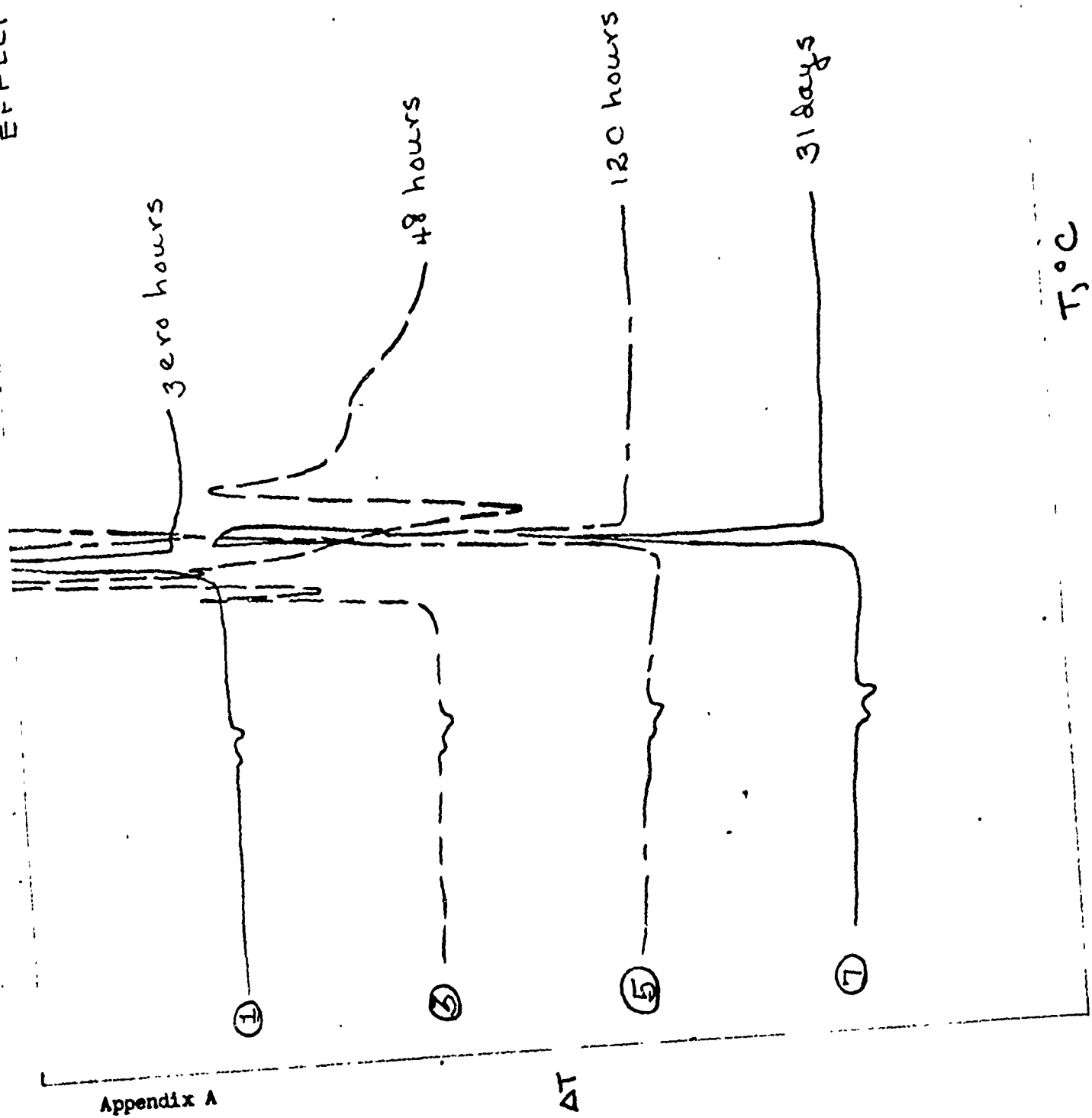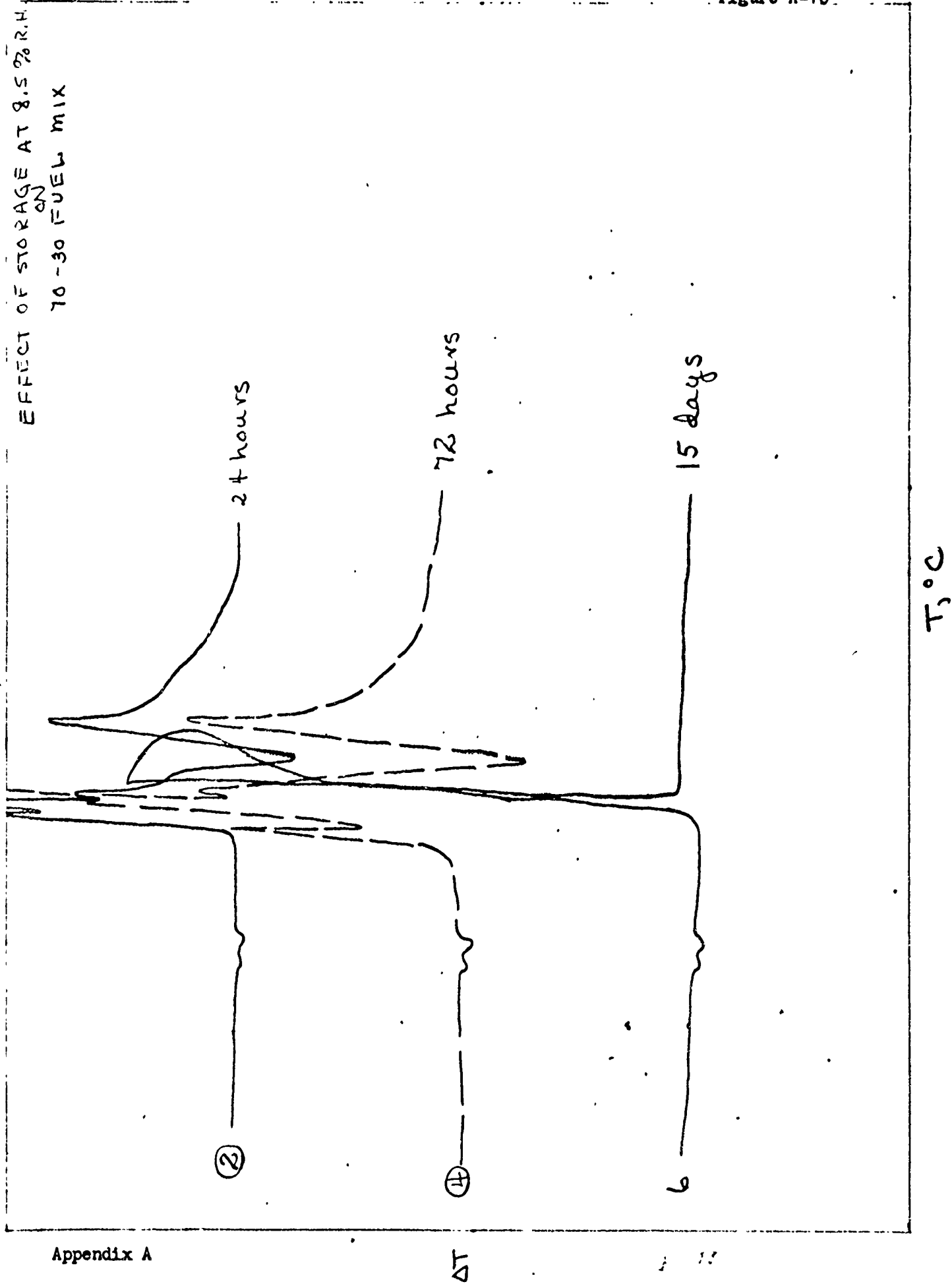
Appendix A

Figure A-11

EFFECT OF STORAGE AT 41.2% R.H
ON
70-30 FUEL MIX

24 hours

72 hours

15 days

T, °C

ΔT

Appendix A

EFFECT OF STORAGE AT 88 8% R.H.
ON
70-30 FUEL MIX

Zero hours

48 hours

120 hours

31 days

①

③

⑤

⑦

T, °C

ΔT

A 14

EFFECT OF STORAGE AT 82.6 %RH
ON
70-30 FUEL MIX

24 hours

72 hours

15 days

②

④

⑦

ΔT °C

T, °C

Figure A-14

Appendix A

EFFECT OF STORAGE AT 97.5% R.H
ON
70-30 FUEL MIX

zero hours

48 hours

120 hours

T, °C

ΔT

(1)

(3)

(5)

Appendix A

EFFECT OF STORAGE AT 97.5% R.H.
ON
70~30 FUEL MIX

24 hours.

72 hours

②

④

T,°C

ΔT

Appendix A

EFFECT OF STORAGE AT 100% R.H.
ON
70-30 FUEL MIX

Zero hours

48 hours

120 hours

T,°C

ΔT

Appendix A

Figure A-18

EFFECT OF STORAGE AT 100% R.H.
ON
70-30 FUEL MIX

24 hours

72 hours (sample detonated pushing thermocouple out of sample tube).

T,°C

ΔT

Appendix A

Figure A-19

Defined Reactivity versus 1/t

Appendix A

Figure A-20

Defined Reactivity
Versus 1/t

1/t hrs.

Reactivity (x10⁵)

Appendix A

APPENDIX B

SOLUTION OF HEAT EQUATION

The general method for the differentiation of a definite integral is as follows. Let F (α) be defined as

$$F(\alpha) = \int_{a(\alpha)}^{b(\alpha)} f(x,\alpha)\, dx \quad (1)$$

then $\dfrac{dF}{d\alpha}$ is given by

$$\frac{dF}{d\alpha} = \int_{a(\alpha)}^{b(\alpha)} \frac{d}{dx} f(x,\alpha)\, dx + \frac{db}{d\alpha} f(b(\alpha),\alpha) - \frac{da}{d\alpha} f(a(\alpha),\alpha) \quad (2)$$

We note that in our solution (eq'n 44) the e^{-z^2} is not a function of the variables x and t, nor is it the lower limit of the integral. Therefore, we can drop the first and third terms in equation 2 to get
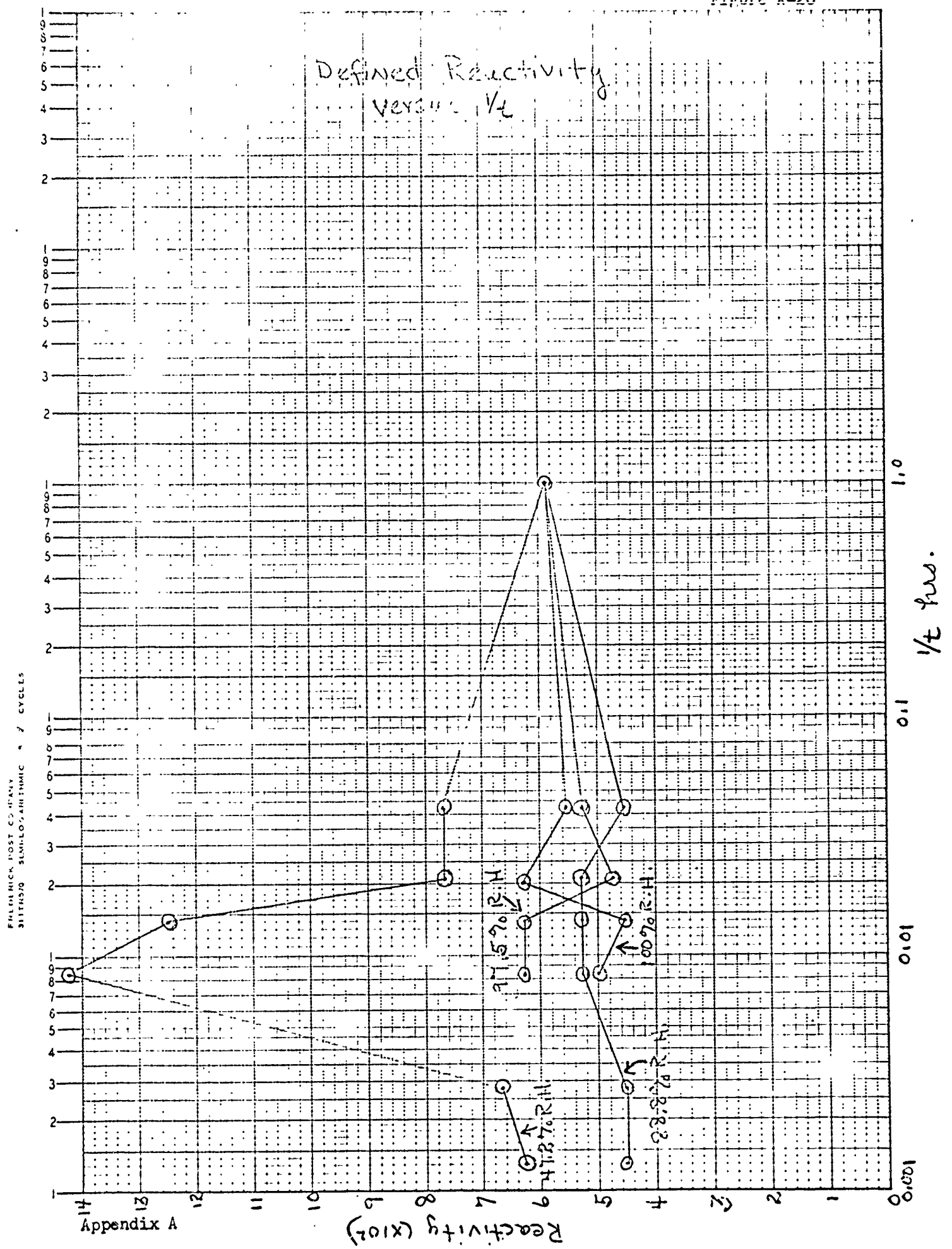
$$\frac{dF}{d\alpha} = \frac{db}{d\alpha} f(b(\alpha),\alpha) \quad (3)$$

Applying equation 3 to calculate $\dfrac{\partial T}{\partial t}$ and $\dfrac{\partial^2 T}{\partial x^2}$ we get

$$\frac{\partial T}{\partial t} = \frac{2}{\sqrt{\pi}} \left(-\frac{1}{2}\right) \left(\frac{x}{2\alpha^{1/2} t^{3/2}}\right) e^{-\frac{x^2}{4\alpha t}} \quad (4)$$

and

$$\frac{\partial T}{\partial x} = \left(\frac{2}{\sqrt{\pi}}\right) \left(\frac{1}{2\sqrt{\alpha t}}\right) e^{-\frac{x^2}{4\alpha t}}$$

$$\frac{\partial^2 T}{\partial x^2} = \alpha \left(\frac{2}{\sqrt{\pi}}\right) \left(\frac{1}{2\sqrt{\alpha t}}\right) \left(\frac{-2x}{4\alpha t}\right) e^{-\frac{x^2}{4\alpha t}} \quad (5)$$

If we multiply equation 5 by an α we get

$$\alpha\left(\frac{\partial^2 T}{\partial x^2}\right) = \alpha \left(\frac{2}{\sqrt{\pi}}\right) \left(\frac{-x}{4\alpha^{3/2} t^{3/2}}\right) e^{-\frac{x^2}{4\alpha t}}$$

$$= \left(\frac{2}{\sqrt{\pi}}\right) \left(\frac{-x}{4\alpha^{1/2} t^{3/2}}\right) e^{-\frac{x^2}{4\alpha t}} \quad (6)$$

Comparing equation 6 to equation 4 we see that they are the same and thus equation 44 is proven to be a solution of the heat equation.

APPENDIX C

APPENDIX C

Ignition Bibliography

References

1. Adler, J., and J.W. Enig. "The Critical Conditions in
   Thermal Explosion Theory With Reactant Consumption,"
   COMBUST FLAME, Vol. 8, No. 2 (June 1964), pp. 97-103.

2. Allen, H., Jr., and M.L. Pinns. Relative Ignitibility
   of Typical Solid Propellants with Chlorine Trifluoride.
   Washington, D.C., National Aeronautics and Space Ad-
   ministration, January 1963. (NASA Technical Note D-1533).

4. Anderson, R., et. al. Critical Comparison of Solid Pro-
   pellant Ignition Theories. Sunnyvale, Calif., United
   Technology Center, August 1963. (TM-34-63-U2).

5. Anderson, R., R.S. Brown, G.T. Thompson, R.W. Ebeling.
   "Theory of Hypergolic Ignition of Solid Propellants".
   Presented at the American Institute of Aeronautics and
   Astronautics, Heterogeneous Combustion Conference, Palm
   Beach, Florida, 11-13 December 1963. (AIAA Preprint
   63-514)

7. Anderson, R., R.S. Brown, and L.J. Shannon. "Ignition
   Theory of Solid Propellants". Presented at American
   Institute of Aeronautics and Astronautics, Solid Pro-
   pellant Rocket Conference, Palo Alto, Calif., 29-31
   January 1964. (AIAA Preprint 64-156).

8. Baer, A.D., N.W. Ryan, and D.L. Salt. "Propellant Igni-
   tion by High Convective Heat Fluxes". Presented at the
   American Rocket Society Solid Propellant Rocket Confer-
   ence, Princeton, N.J., Princeton University, 28-29 Janu-
   ary 1960. (ARS Preprint 1059-60). Also in "Progress in
   Astronautics and Rocketry. Vol. 1, Solid Propellant
   Rocket Research". New York, Academic Press, Inc.,
   pp. 653-72.

9. Baer, A.D., and N.W. Ryan. "Ignition of Composite Pro-
   pellants by Low Radiant Fluxes," AIAA Journal, Vol. 3,
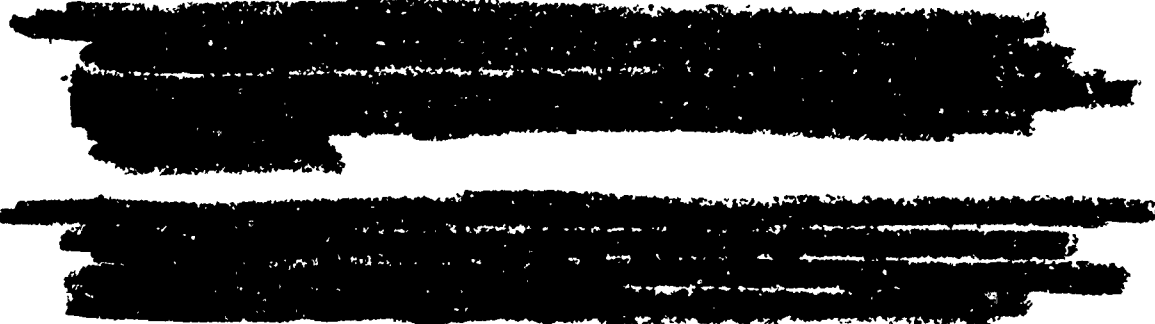   No. 5 (May 1965), pp. 884-89.

10. Baer, A.D. Ignition of Composite Rocket Propellants. Salt Lake City, Utah, University of Utah, Department of Chemical Engineering, August 1965. (Unpublished Ph.D. thesis).

11. Bamford, C.H., J. Crank, and D.H. Malan. "The Combustion of Wood", PROC CAMBRIDGE PHIL SOC, Vol. 42 (1946), pp. 166-82.

13. Beyer, Rodney B., and Norman Fishman. "Solid Propellant Ignition Studies with High Flux Radiant Energy as a Thermal Source". Menlo Park, Calif., Stanford Research Institute, in Progress in Astronautics and Rocketry, Vol. 1, Solid Propellant Rocket Research. Academic Press, 1960. pp. 673-92.

14. Beyer, R.S., R. Anderson, R.O. MacLaren, and W.J. Corcoran. Ignition of Solid-Propellant Motors Under Vacuum. Sunnyvale, Calif., United Technology Center, 8 April 1965. (Final Report UTC-2079-FR, Contract No. Af 04(611)-9701).

15. Blanchard, R., and H. Bouchon. On the Initiation of Explosives by Light: Theoretical Results. Paris, France, Commissariat a l'Energie Atomique (Informal Memorandum received by private communication).

16. Boddington, T. The Initiation of Explosion by an Intense Light Flash. Cambridge, England, Laboratory for the Physics and Chemistry of Solids, Cavendish Laboratory, 1963.

17. Bradley, H.H., Jr., and E.W. Price. Tables of Computer Calculations for Heating of an Opaque, Semi-Infinite Reactive Solid by Constant Radiant Flux, Ignoring Reactant Consumption. China Lake, Calif., U.S. Naval Ordnance Test Station, December 1963. (Unpublished Technical Note TN 5008-17, Research Department, Aerothermochemistry Group. Computer solutions carried out by Stanford Research Institute).

18. --------. Tables of Computer Calculations for Heating of a Reactive Solid by Constant Radiant Flux, Including Effect of Depletion of Reactant by Chemical Reaction of Order 1/2, 1, and 3/2. China Lake, Calif., July 1964. (Unpublished Technical Note TN 5008-18, Research Department, Aerothermochemistry Group. Computer soluti s carried out by Stanford Research Institute).

19. Bradley, H.H., Jr., and E.W. Price. Tables of Computer
    Calculations for Heating of a Reactive Solid by Constant
    Radiant Flux, Including Effects of Depletion of Reactants
    and of Optical Absorption of Radiant Energy in Depth.
    China Lake, Calif., August 1964. (Unpublished Technical
    Note TN 5008-19, Research Department, Aerothermochemistry
    Group. Computer solutions carried out by Stanford Re-
    search Institute).

20. Carslaw, H.S., and J.C. Jaeger. Conduction of Heat in
    Solids, 2nd ed. London, Oxford Univ. Press, 1959, p. 284.

21. Cook, G.B. "Developments in the Theory of Thermal Ex-
    plosions". Presented at the Sixth Symposium (Interna-
    tional) on Combustion, Yale University, New Haven, Connec-
    ticut, 19-24 August 1956. New York, Reinhold Publishing
    Corporation, pp. 626-31.

22. Crank, J., and P. Nicholason. "A Practical Method for
    Numerical Evaluation of Solutions of Partial Differen-
    tial Equations of the Heat-Conduction Type", PROC CAMBRIDGE
    PHIL SOC, Vol. 43 (1947), pp. 50-67.

23. DeSoto and Friedman. AIAA Journal 3, 405-12 (1965).

24. Evans, Marjorie W., Rodney B. Beyer, and Leonard McCulley.
    "Initiation of Deflagration Waves at Surfaces of Ammonium
    Perchlorate", J. CHEM PHYS, Vol. 40, No. 9 (1 May 1964),
    pp. 2431-38.

25. Frank-Kamenetskii, D.A. Diffusion and Heat Exchange in
    Chemical Kinetics, Princeton University Press, (Trans-
    lation) 1955.

26. Frazer, J.H. and Hicks, B.L., J. Phys.and Colloid Chem.
    54 872-76 (1950).

27. Hermance, C.E., R. Shinnar, J. Wenograd, and M. Summerfield.
    Solid Propellant Ignition Studies: Ignition of the Reaction
    Field Adjacent to the Surface of a Solid Propellant.
    Princeton, J.J., Princeton University, 1 December 1963.
    (Aeronautical Engineering Report No. 674, Grant AF-AFOSR-
    92-63).

28. Hermance, C.E., R. Shinnar, and M. Summerfield. "Igni-
    tion of an Evaporating Fuel in a Hot, Stagnant Gas Con-
    taining an Oxidizer", American Institute of Aeronautics
    and Astronautics, AIAA J, Vol. 3, No. 9 (September 1965),
    pp. 1584-92.

29. --------. "Ignition Theory of an Evaporating Fuel in a
    Hot Oxidizing Gas, II". (Personal communication: M.
    Summerfield to E.W. Price, November 1965).

30. Hicks, Bruce L. "Theory of Ignition Considered as a
    Thermal Reaction", J CHEM PHYS, Vol. 22, No. 3 (March
    1954), pp. 414-29. See also Hicks, B.L., J.W. Kelso,
    and Julian David. Mathematical Theory of the Ignition
    Process Considered as a Thermal Reaction. Aberdeen,
    Md., Aberdeen Proving Ground, Ballistic Research Labora-
    tories, July 1951. (Report No. 756).

31. Hightower, J.D. Minutes of the Third Arc-Image Sym-
    posium. China Lake, Calif., U.S. Naval Ordnance Test
    Station, 10 August 1965. (Memo 5008/JDH:bjm Serial
    001).

32. Keller, J.A., Baer, A.D. and Ryan, N.W., Fall Meeting
    Combustion Inst. 1964.

33. Keller, J.A., C.P. Richardson, A.D. Baer, and N.W.
    Ryan. Final Technical Report on Propellant Ignition
    by Convective Heat Fluxes. Salt Lake City, Utah,
    University of Utah, Department of Chemical Engineering,
    28 June 1963 to 30 September 1964. (Contract N60530-
    9060 USNOTS).

34. Kuchl, Donald H. AIAA Journal 3 2239-47 (1965).

35. Landau, H.D. "Heat Conduction in a Melting Solid",
    QUART APPL MATH, Vol. 8 (1950), pp. 81-94.

36. Lovine, R.L., L.Y. Fong, and B.E. Paul. "Diffusional
    Analysis of Composite Propellant Ignition and Its
    Application to Solid Rocket Ignicion". Presented at
    American Institute of Aeronautics and Astronautics,
    Solid Propellant Rocket, Conference, Palo Alto, Calif.,
    29-31 January 1964. (AIAA Preprint 64-117).

37. McAlevy, R.F., III, P.L. Cowan, and M. Summerfield.
    "The Mechanism of Ignition of Composite Propellants
    by Hot Gases". Presented at the American Rocket
    Society Solid Propellant Rocket Conference, Princeton,
    N.J., Princeton University, 28-29 January 1960. (ARS
    Preprint 1058-60). Also in "Progress in Astronautics
    and Rocketry, Vol. 1, Solid Propellant Rocket Research".
    New York, Academic Press, Inc., pp. 623-52.

38. McAlevy, R.F., III, and M. Summerfield. "Ignition of
    Double-Base Solid Rocket Propellants", AM ROCKET SOC,
    J, Vol. 32 (1962), pp. 270-73.

39. McAlevy, R.F., III, and J.G. Hansel. "Linear Pyrolysis
    of Thermoplastics in Chemically Reactive Environments."
    AIAA JOURNAL, Vol. 3, No. 2 (February 1965) pp. 243-9.

40. McAlevy, R.F., III, S.Y. Lee, and R.S. Magee. "The
    Solid Propellant Ignition Mechanism: A Simple Diagnostic
    Experiment", ASTRONAUTICA ACTA, Vol. II, No. 2 (1965),
    pp. 144-45.

41. Mitchell, Rex C., John A. Keller, Alva D. Baer, and Norman W. Ryan. Ignition of Solid Propellants. Salt Lake City, Utah, University of Utah, Department of Chemical Engineering, 1962. (AFOSR 62-99).

42. Niessen, W.R., and E.K. Bastress. Solid Propellant Ignition Studies, Cambridge, Massachusetts, Arthur D. Little, Inc. 15 July 1965. (First Quarterly Report Technical Documentary Report No. AFRPL-TR-65-136. Prepared under Contract AF04(611)-10741).

43. Olds, Robert H., and Gail B. Shook. Mathematical Study of Thermal Processes Relating to Reaction Rates in Solid Fuels. China Lake, Calif., U.S. Naval Ordnance Test Station, 30 June 1952. (Tech. Memo. 917).

44. Pearson, G.S. and Sutton, D. AIAA Journal 4, 954 (1966).

47. Price, E.W., H.H. Bradley, Jr., and R. Fleming. "Ignition of Solid Propellants". Presented at the Meeting of the Western States Section of the Combustion Institute, San Diego, Calif., 29-30 April 1963 (Paper No. WSS/CI 63-6).

48. Price, E.W., H.H. Bradley, Jr., J.D. Hightower, and R.O. Fleming, Jr. "Ignition of Solid Propellants". Presented at the American Institute of Aeronautics and Astronautics Solid Propellant Rocket Conference, Palo Alto, Calif., 29-31 January 1964. (AIAA Preprint No. 64-120).

49. Roth, James F., and George P. Wachtell. "Heat Transfer Kinetics in the Ignition of Solid Propellants", IND ENG CHEM FUNDAMENTALS, Vol. 1, No. 1 (February 1962), pp. 62-7.

50. Salzman, P.K., Irwin, O.R. and Anderson, W.H., AIAA Journal 3, 2230, (1965).

51. Sims, D.L. "Damage to Cellulosic Solids by Thermal Radiation", COMBUST FLAME, Vol. 6 (December 1962), pp. 303-18.

52. Squire, William, and Connie Foster. A Mathematical Study of the Mechanism of Wood Burning. San Antonio, Texas, Southwest Research Institute, 3 February 1961. (Tech. Progress Report No. 1, Contract No. CST-362, SWRI Project No. 1-965-2).

53. Squire, William. "A Mathematical Analysis of Self-Ignition", COMBUST FLAME, Vol. 7, No. 1 (March 1963), pp. 1-8.

54. Summerfield, M., and R.F. McAlevy. "The Shock Tube as a Tool for Solid Propellant Ignition Research", JET PROPULSION, Vol. 28 (1958), pp. 478-81.

55. Thomas, P.H. "Effect of Reactant Consumption of the Induction Period and Critical Conditions for a Thermal Explosion", ROY SOC LONDON, PROC, Vol. 262A(1961), pp. 192-206.

56. Thomas, P.H., and P.C. Bowes. "Some Aspects of the Self-Heating and Ignition of Solid Cellulosic Materials", BRIT J APPL PHYS, Vol. 12 (May 1961), pp. 222-29.

57. von Elbe, Guenther. "Theory of Solid Propellant Ignition and Response to Pressure Transients", in Bulletin of the Interagency Solid Propellant Group Meeting, Alexandria, Va., Atlantic Research Corporation, July 1963, Vol. III, pp. 95-127.

58. Weatherford, W.D., Jr. A Mathematical Study of the Mechanism of Wood Burning. San Antonio, Texas, Southwest Research Institute, January 1962. (Tech. Progress Report No. 2, Contract No. CST-362).

59. Williams, F.A., and M. Barrere. "Ignition of Solid Propellants". Presented at the Second Interagency Chemical Rocket Propulsion Group Combustion Conference, El Segundo, Calif., 1-5 November 1965.

60. Williams, F.A. AIAA Journal 4, 1354-1357, (1966).

63. Zaehringer, A.J.   Solid Propellant Bibliography Jet
    Prop. 900-27 (1957) Section 8.   27 references collected
    under "Ignition".

64. Blanchard, R.   "Initiation thermique des explosifs au
    moyen d'eclairs lumineux.   Etude theorique".   Academic
    des Sciences 2550-53, March 1963.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Washington College Chestertown, Maryland 21620	UNCLASSIFIED
	2b. GROUP N/A

3 REPORT TITLE

EFFECT OF PHASE CHANGE IN SOLID-SOLID REACTIONS

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report - October 1964 to October 1967

5 AUTHOR(S) *(First name, middle initial, last name)*

McLain, Joseph H. and McClure, Michael D.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1968	105	105
8a. CONTRACT OR GRANT NO. DA-AMC-18-035-77(A) b. PROJECT NO. 1C014501B71A c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) WCDC 6667 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* N/A

10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Commanding Officer, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010.

| 11 SUPPLEMENTARY NOTE
 Life Sciences Basic Research in Support of Material, Chemical (U). | 12. SPONSORING MILITARY ACTIVITY
 Edgewood Arsenal Research Laboratories
 Edgewood Arsenal, Maryland 21010
 (H.A. Brown, Proj. O., Ext 22166) |

13 ABSTRACT The effects of phase changes, defect structure, mechanical treatment, moisture content and doping of the constituents of the potassium chlorate-sulfur system on the reactivity of the system was investigated by means of differential thermal analysis, thermoconductimetric analysis and burning rate studies. The effect of confinement during burning of the fuel mis (potassium chlorate, sulfur and sodium bicarbonate) was also investigated.

It was found that the mechanism of the KClO3-S reaction is independent of the decomposition of the KClO3, but is dependent upon the lattice "looseness" of the KClO3 and its permeability to the sulfur molecules. It was also found that previous treatment of the constituents such as mechanical and thermal treatment or the production of certain defect structures have an important effect on the stability of the system. Burning rate studies indicated that the growth of burning to detonation in the fuel mix is profoundly enhanced by a large K factor in the munition.

14. KEYWORDS

Pyrotechnics	Mechanical activation Potassium chlorate
Differential thermal analysis	Activation energy Sulfur
Thermoconductimetric analysis	Hedvall effect
Burning rates	K factor
Ignition temperature	Doping
Ignition energy	Heat of Reaction

DD FORM 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.